The Royal Society
of Canada

PATHWAYS, CYCLING AND TRANSFORMATION OF LEAD IN THE ENVIRONMENT

EDITED BY
PAMELA M. STOKES

THE COMMISSION ON LEAD IN THE ENVIRONMENT

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THE ROYAL SOCIETY
OF CANADA

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PREFACE

This is one of three complementary volumes of scientific papers that the Royal Society of Canada's Commission on Lead in the Environment used extensively in preparing its final report, Lead in the Canadian Environment: Science and Regulation.

The present volume deals with the pathways taken by lead in its movement through the environment towards human targets. The second contains papers dealing with the health effects of lead. In addition to material presented at the Commission's workshops, both volumes contain syntheses of the matters under discussion, written by their respective editors or by individual Commissioners.

The third volume is a technical appraisal of the health effects and industrial and engineering problems inherent in the alternative lead-free ways of matching fuels to engines.

The Society is grateful to all the individual contributors whose views are expressed in these documents. They are also entitled to all the credit due for their labours.

F. Kenneth Hare
Chairman

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ABBREVIATIONS

a	annum (year)
AAS	atomic absorption spectrometry
ALA-D	δ-aminolaevulinic acid dehydratase
asv	anodic stripping voltammetry
BCF	bioconcentration factor
CEC	cation-exchange capacity
CF	concentration factor
CNS	central nervous system
d	day
DTPA	diethylenetriaminpentaacetic acid
EDTA	ethylenediaminetetraacetic acid
EEC	European Economic Community
EF	enrichment factor
GC	gas chromatography
h	hour
HPLC	high-performance liquid chromatography
ICP	inductively coupled plasma
ICRP	International Commission on Radiological Protection
ILE	Isotopic Lead Experiment
IW	interstitial water
MIP	microwave-induced plasma
NASN	National Air Surveillance Network
PbA	air lead
PbB	blood lead
PbD	dust lead
PbF	lead fall-out rate
PbS	soil lead
PCA	principal component analysis
ND	not detectable
s	second
SEM	scanning electron microscopy
TL	threshold level
TLC	thin-layer chromatography

1. OVERVIEW OF THE WORKSHOP ON PATHWAYS, CYCLING AND TRANSFORMATION OF LEAD IN THE ENVIRONMENT

Pamela M. Stokes

Commission on Lead in the Environment
Toronto

A workshop was convened by the Royal Society of Canada Commission on Lead in the Environment in October 1985, in Edmonton Alberta. Participants at the workshop submitted papers which have been reproduced here with very little scientific editing. This overview summarizes and integrates the major points which were made by the respective authors, but does not review any of the literature beyond the papers in this volume.

In describing global cycling, Nriagu (p. 17) shows that 27% of all man's lead consumption recorded over time has occurred in the two most recent decades. Alkyllead compounds in gasoline represent a major component of the mobilization of lead from the lithosphere to the biosphere via the atmosphere. Canada is a significant contributor of lead to the biosphere, with total emissions of 10×10^6 g a^{-1} to the atmosphere, compared with 331×10^6 g a^{-1} over the entire globe. Concentrations of lead in the atmosphere in pre-technological times were probably less than 0.1 ng m^{-3}, but present-day concentrations even in the most remote areas can sometimes exceed several nanograms per cubic metre.

The turnover of lead in the atmosphere is rapid (40 times per year), with a mean residence time in the northern hemisphere of 10 d. This means that the concentration of lead in the atmosphere is not a good measure of the anthropogenic mobilization of lead in the environment, as the atmosphere serves merely as a "conveyor belt". Nriagu proposes that lead fall-out rate (PbF) is better than lead in air as a measure of the environmental lead burden. Chamberlain (p. 379) also refers to the usefulness of PbF in the context of determining lead uptake by children. Unfortunately, according to Nriagu, few data for this parameter PbF are available for locations in Canada.

The atmosphere is the major source of lead for the oceans, as evidenced by the consistently higher concentrations of lead in surface layers of sea water compared with deeper waters. Similarly, for soils, anthropogenic lead in the atmosphere is the major source, with a flux to soil of 60-200 mg m^{-2} a^{-1} in urban areas, compared with 6-30 mg m^{-2} a^{-1} in rural areas. As a result of this, soil lead levels in many urban areas are 1-4 orders of magnitude above background, even excluding soils contaminated by local point sources.

Nriagu identifies a neglected area of possible concern, that of contamination of fresh water by lead. The reservoir of lead in fresh water is very small compared with the anthropogenic input, suggesting that pollution of surface waters may be more severe than has generally been realized. This aspect is taken up in later sections, particularly by Luoma (p. 185) and by Hodson (p. 203), who emphasize the massive flux of lead from water to sediment, and discuss the implication of this for sediment-dwelling organisms and for consumers of these benthic feeders.

The chemistry of lead in air is addressed by Van Loon (p. 37), who provides a critical review of methods and the quality of data for lead in air. His particular emphasis is on the so-called speciation of the different chemical forms of lead in the atmosphere. He recommends the use of microwave-induced plasma emission spectrometry combined with gas chromatography for developing a highly specific and sensitive methodology to determine individual chemical species. He also addresses the potential power of isotopic ratios to aid in source identification for lead, and considers that the best approach in this context is inductively coupled plasma mass spectrometry. In discussions at the workshop (not recorded here), several participants felt that source identification was often confounded by the multiple sources of lead, so that isotopic ratios might be difficult to interpret. Puckett (p. 225), in his discussion of biological monitors of terrestrial lead deposition, also refers to the use of isotope composition in sources and in receptors (in his example, lichens and mosses are the receptors) as a means of source identification. Van Loon emphasizes the need for comprehensive quality assurance programmes in all laboratories doing trace lead determinations, as well as the need for better detection limits for determination of lead or lead species in air.

It is clear from the review of Van Loon that methods for measuring speciation of lead in air are still at an early stage of development. Certainly they will not be available as routine tools for some time to come.

Davidson (p. 53) discusses the spatial and temporal trends for lead in air, and he, like Van Loon, advises caution in accepting data prior to the early 1970s. Not only were the analytical methods poorly developed, but the extent of problems related to contamination was scarcely recognized until quite recently. Lead in urban air generally ranges in concentration from 1 to 10 $\mu g\ m^{-3}$, and from 0.1 to 1 $\mu g\ m^{-3}$ in rural areas. Because of the technical problems, values for early dates (pre-1970) may be too high.

Lead from combustion sources occurs predominantly in the submicrometre fraction of particulates in the atmosphere; in this form it is slow to be deposited, and therefore travels long distances. As a result, similar size distribution for lead in air is found in urban, non-urban continental and marine sites. The overall mass median aerodynamic diameter for lead is 0.55 μm, compared with 3.8 and 4.5 μm for sodium and aluminum, respectively, which come mainly from crustal and sea-spray sources.

Davidson proceeds to relate size distribution of lead in air to deposition in the human lung and to dry deposition onto natural surfaces. Calculations suggest that in the pulmonary region, efficiency of lead deposition may be as high as 26%, but in the tracheobronchial or nasopharyngeal regions, efficiencies may be less than 10%. Deposition of lead, in the dry from, onto natural surfaces such as plants is quite small because of the small particle size. Measurement of dry deposition continues to be technically unsatisfactory, although newly developed techniques involving direct measurement on vegetation and on aerodynamically designed surfaces show promise for future monitors.

Deposition is of course only the preliminary stage of biological uptake from the atmosphere. Later in the proceedings, discussions by Chamberlain (p. 379) and Elias (p. 359) address the subsequent uptake of inhaled lead into man's tissues, and Puckett (p. 225), Steinnes (p. 257), Chaney et al. (p. 301), Ter Haar (p. 339) and Thornton (p. 267) all make reference to the atmosphere as a source of lead for plants. In a few examples, animal uptake is also addressed.

In the absence of reliable historical data on lead in air, past trends in time usually have to be determined indirectly. Soils, sediments and peat can provide such indirect evidence, and Norton and Kahl (p. 97) address lake sediments and peat in this context. They show that lead concentrations in cores of lake sediment and peat can be used to calculate such trends. Net rates of accumulation, based on this approach, exceed loading rates for wet deposition. This suggests that dry-fall, fog and cloud moisture are important sources for total lead loading to the earth. Lake sediment lead is representative of lead collected by the lake surface, rather than by the entire watershed, because lead deposited on the terrestrial system is quite immobile except under very extreme conditions. (This is in contrast to the situation for some other metals.) Records in lake sediment and peat indicate at least 100 years of elevated atmospheric deposition, with values increasing until the late 1970s, but with recent (10-15 years) decreases in net accumulation rates for most parts of eastern North America, suggesting a decline in atmospheric deposition in recent years.

Norton and Kahl discuss the limitations of the reconstructions based on sediment and peat data, but there is little doubt that these palaeolimnological methods are the best means at our disposal for estimating historical trends and for identifying sources. When combined with other geochemical and biological data, these techniques yield quite impressive results.

While the total amount of lead in sediment at a given time, or in a given layer, can give information about its loading into the aquatic system, the availability of this lead and thus its potential to affect biota, or to cycle through the system, cannot normally be predicted from a measurement of total lead. Campbell and Tessier (p. 133) address the partitioning of lead in sediments among dissolved and particulate phases. Most schemes for speciation of sediment lead depend upon extraction, usually sequential extraction, by leaching agents which remove progressively more strongly bound and presumably less readily available forms of the metal. Theoretical equilibrium models are at present less useful than this practical, albeit operationally defined, method for chemical speciation of lead in sediment. Lead levels in benthic invertebrates from both marine and freshwater systems are better related to lead in one of the weakly bound (easily extracted) fractions than to total lead in sediment. Campbell and Tessier point out that this does not necessarily imply that the main route for lead uptake is from particulate material; the relationship could be explained by absorptive control of dissolved lead in the interstitial water. As far as absorption is concerned, the presence of amorphous iron oxyhydroxide decreases the uptake of lead by invertebrates.

For aquatic plants rooted in sediment, studies have shown that metal uptake can be affected by pH, redox potential, organic matter and amorphous iron oxyhydroxides. Plants, unlike benthic invertebrates, can take up only dissolved lead, but the factors listed can affect both the chemical form of the lead and the uptake or transport mechanisms. For both plants and animals, there are relatively few studies which attempt to relate the forms of lead in sediment to the metal burdens or the metal effect for biota.

Thus, for empirical relationships which would enable certain predictions to be made concerning plant or animal uptake of lead from sediment, much more information is required. As far as understanding the relationship between chemical forms and biological uptake is concerned, Luoma (p. 185) notes that our ability to predict the fate of lead and its effects on biota is limited by our present inadequate understanding of many aspects of the biological mechanisms. Ideally, studies of geochemical forms and of biological uptake of lead, as for other metals, should be co-ordinated as they have been in a few instances cited by Campbell and Tessier (p. 133).

As shown for sediments, several different chemical species of lead exist in the aquatic system. For the dissolved phase, the same is true, and the ability of chemists to determine and distinguish between forms of organic lead in the environment has advanced quite rapidly in recent years. The organic forms of lead include those which are toxic to biota. Chau (p. 171) describes the forms and possible origins of organolead in water, and identifies tetraalkylleads, mainly in their use as antiknock additives to gasoline, as the most important source of lead pollution in the environment. Degradation of tetraalkylleads to tri- and dialkyllead and Pb(II) is relatively slow, with half-lives ranging from 3 h to 60 d for different forms. All three forms of alkyllead are concentrated in fish tissue, with the lipophilic non-polar tetraalkyllead having a high affinity for the lipid layer of fish intestine. Later in the proceedings, Hodson (p. 203) and Luoma (p. 185) each discuss the tendency of lead to bioaccumulate. The high affinity of the tetraethyllead for tissues is associated with a toxicity to aquatic biota generally 10-20 times greater than that of inorganic lead.

The analytical determination of alkyllead in plant or animal tissue can now be accomplished with the aid of a suitable solubilizer, tetramethylammonium hydroxide, which brings the lead into solution without altering the chemical forms. Advances in the determination of the ionic alkyllead species in water have resulted from very recent work, mainly by Chau and his group, on a method which uses a chelator followed by butylation, with gas chromatography and atomic absorption spectrophotometry for detection. Chau concludes that "a sensitive and specific method for complete speciation analysis of all molecular and ionic alkyllead compounds is now available for environmental studies".

Chau also addresses the process of methylation of Pb(II) compounds, and cites 10 studies since 1975 which have positive results in this respect, compared with 5 studies which have negative results. Clearly this is a controversial area, in contrast to the methylation of Pb(IV) compounds, a process whose occurrence in the environment is accepted by all workers concerned. The mechanisms (biotic or abiotic) and the quantitative significance of lead methylation in the environment are still very uncertain. The general consensus of the workshop was that environmental methylation of lead was not quantitatively very important in the overall picture. With the exception of situations where there is anthropogenic release of organoleads to water, the occurrence of these toxic compounds in aquatic systems is probably not significant for biota.

Luoma (p. 185) considers the processes involved in the transfer of lead from the environment into the aquatic food-chains, and introduces the concept of the partitioning of lead into different forms in sediments, i.e. the speciation of lead within the solid phase as well as in the aqueous phase. He stresses that factors such as dissolved organic carbon and nutrient concentrations, as well as the chemical speciation of lead, influence its uptake by biota. It is clear from a number of studies in freshwater as well as marine systems that lead is not biomagnified through the food-chain, but rather that it tends to decrease in concentration at successive trophic levels. This is in contrast to mercury, and implies that lead is less hazardous than some other metals to aquatic biota. Nevertheless, sediment-dwelling (benthic) organisms which ingest solid material can achieve quite high body burdens of lead. As a result, food items for man, such as certain soft-shelled clams, may contain concentrations of lead as high as that in paint chips. On the other hand, there is great interspecific variation with respect to lead in benthic animal tissue; oysters, for example, accumulate very much less lead than do certain clams. Fish tissue generally contains rather low concentrations of lead, below the regulatory level. Thus this route to man could be a significant vector for lead, but only in rather special cases, and these are not readily predictable.

Luoma also discusses the use of bioindicators or sentinel species, and cites the example of the Mussel Watch, a rather comprehensive study of lead (as well as other metals) which includes a survey of lead in mussels at 29 stations along the west coast of the United States. Levels for southern California consistently exceeded those for central California, but even the highest levels in this study were only 5% of those observed for mussels in mining regions elsewhere in the world. Luoma emphasizes the need to understand the chemical and biological processes related to lead transfer from sediments (the largest repository of lead) to biota. But, even with our present incomplete state of knowledge, he considers that certain species of aquatic organisms could be used as indicators to identify lead-contaminated environments and establish threshold limits for environmental lead contamination.

The toxic effects of lead on algae, invertebrates and fish are addressed by Hodson (p. 203). The literature reveals that the concentrations of total waterborne lead that are toxic to aquatic biota range from almost 4.0 to 500,000 $\mu g\ L^{-1}$! Hodson shows that the most important causes of this variation include organic and inorganic complexation, the form of lead (whether Pb(II) or Pb(IV)), the respective sensitivity of different species and the age of the exposed organism. Bioconcentration factors (ratio of tissue lead to water lead) range from less than 1000 to 20,000. The highest values are for plants, and there is repeated confirmation that lead is not biomagnified in food-chains.

Symptoms of lead toxicity for fish include lead accumulation (especially elevated blood lead), enzyme inhibition (ALA-D is inhibited by lead in fish, just as it is in mammals), deformities and reproductive effects.

In the field, the enzyme inhibition and elevated blood lead demonstrated in laboratory studies are observed in relation to elevated lead in water or sediment, but a clear dose-response relationship has yet to be obtained. Benthic fish species are more contaminated with lead than are pelagic species from the same sites, and in some instances edible portions of fish exceed the recommended limit for human health. For the most part, because lead is not accumulated in muscle but rather in blood, liver and kidney, human consumers of fish are not at risk.

The most important research need, in Hodson's opinion, is the evaluation of the fate and effects of alkyllead compounds, particularly of their entry into human food.

The second day of the workshop addressed the pathways and fate of lead in the terrestrial system. In a consideration of the spatial and temporal trends of lead in the atmosphere, Puckett (p. 225) shows how lower plants (lichens and bryophytes) have considerable potential for use in regular surveillance of lead in deposition and to some extent in quantification of the pollutant. By comparing biological with physical measurements of lead, some examples indicate good empirical relationships between lead deposition and lead levels in lower plants, and results for lead are better than those for some other elements. This is probably because lead is rather immobile and insoluble. Plant monitors have also been used in source identification, with the use of enrichment factors which utilize the ratio of the element of concern to a conservative element such as scandium in crustal rock, compared with the same ratio in the plant.

Examples of the use of lower plant monitors which have been used to determine spatial and temporal distribution for line sources, point sources and remote sources come from Europe, Scandinavia and North America. The studies which are selected by Puckett support the validity of the approach. The properties of these lower plants mean that stored (herbarium) specimens can be retrieved and used to estimate metal loadings in earlier times. One study from Sweden has shown that a moss (Sphagnum) appears to be reflecting the recent general decline of lead emissions from the mid-1970s into the 1980s.

Steinnes (p. 257) addresses lead contamination of the terrestrial environment from long range transport using the moss Hylocomium splendens, and shows that domestic sources of lead as well as many other pollutants in Norway are small compared with those from outside Norway. He suggests that Canada may experience a comparable contribution from neighbours to the south. In terms of reflecting atmospheric deposition, Steinnes shows that the pattern for mosses is very similar to that for soil lead in undisturbed podzols, and that both show a gradient from southern to northern Norway. He also gives data on wild and domestic animals, and describes how lead in the liver of lamb and moose also shows a south-north gradient, reflecting atmospheric deposition. Steinnes, like Norton, supports the use of peat cores from ombrotrophic (receiving only atmospheric inputs) bogs to track the history of lead deposition.

Chaney et al. (p. 301) focus on the risk to urban gardeners of lead in air and lead in soil from a number of sources, but especially automobiles, sewage sludge and paint. They list the following recommendations for limiting metal exposure from urban soils and crops: the prevention of pica; soil tests for gardens and play areas where there is a suspicion of contamination; adequate iron and calcium in the diet of children; restriction of vegetable gardens to at least 50-100 foot from highways; washing and peeling of leafy and root crops, respectively; control of soil pH to 6.5-7.0 with addition of lime and organic matter; and the use of hedges or fences to intercept lead in air from heavy traffic. Chaney et al. do emphasize that ingestion of lead-contaminated soil per se is much more serious in terms of a risk to children than is consumption of vegetables from such soil. The movement of lead from soil into and through plants is quite limited, but direct deposition from air can result in contamination of leafy vegetables and buildup of lead concentrations in soil.

Ter Haar (p. 339) considers that the contribution of airborne lead to food and water is relatively minor, and presents data to show that for every 1000 $\mu g\ g^{-1}$ in soil there is a contribution of less than 1 $\mu g\ dL^{-1}$ of lead in blood for children. He emphasizes that paint is an important contributor to lead in soil, although he agrees that fall-out from air near busy highways can add to natural levels of lead in soils. The often opposing views of Chaney et al. and Ter Haar are symptomatic of the controversy regarding the relationship between soil and air lead, and lead in vegetables, which in turn contributes to the dietary intake of lead by adults and children. This controversy is scientific as well as political in its implications.

Thornton (p. 267) addresses soil and dust as pathways of lead to man, basing much of his information on data from Britain, where many soils have been contaminated by mining activities in the past. Peat profiles for different parts of Britain indicate two major periods of lead contamination: the industrial revolution in the 18th century and the use of lead in motor vehicles since World War II. Overall, British soils have higher lead concentrations than those in the United States, with more than 4000 km^2 contaminated from historical lead mining and smelting. Interestingly, some areas in the United Kingdom with very high soil lead do not show the expected elevations in blood lead. Chamberlain (p. 379) also refers to this difference in blood lead/soil lead relationship between models derived from US data and from actual measurements in the UK, and believes that one explanation for this difference is that deposited lead becomes agglomerated with time, and therefore is less available for direct ingestion.

Thornton refers to the British national surveys of lead in dust, and shows that lead in house dust is related to age of the property, proximity to the road and frequency of house-cleaning, as well as other factors. There is a consistent correlation between lead in soil and lead in dust. Thornton indicates that it is not yet possible to determine the proportional contributions of motor vehicles and paint to lead in dust.

Thornton also describes a wide range of studies and includes a review of data for agricultural soils, which in Britain have a geometric mean lead concentration of 42 $\mu g\ g^{-1}$, compared with 18 $\mu g\ g^{-1}$ for cropland in the United States. Cattle consume lead from soil, and their blood lead reflects soil lead (but not lead in vegetation) in a broad way. However, even on soils with very high lead levels, no ill effects on cattle have been shown. The author suggests that the long industrial history of the United Kingdom may present a special situation that may not be mirrored in other parts of the world with a shorter industrial record. However, results for urban Washington and industrial Baltimore suggest that the differences may not be very great in terms of soil levels, although the effects on humans may still be different because of differences in time since deposition or differences in chemical form of deposited lead.

Thornton describes some interesting modern techniques which are being developed to characterize the respective sources of lead in dust, and refers to the use of scanning electron microscopy with automated image analysis and X-ray energy spectroscopy which, in conjunction with a "library" of information, can aid in source apportionment. At present, however, this method is not developed for general use.

The EPA model for total lead exposure of humans from natural and anthropogenic sources is described by Elias (p. 359). One major objective of this model is to assist in making regulatory decisions by providing data on the fraction of total lead exposure for man that is derived from the atmosphere, from food, from water and from dust, respectively. Elias shows how the model uses a flexible structure that is amenable to changes in either the baseline information or formulae for calculation. The output should be informative from the standpoint of presenting summaries of changes in exposure with any departure from the baseline situation and changes to the baseline exposure expected from any modification of ambient air quality. There was some disagreement from the participants during discussion concerning some of the values for lead in food which were presented.

In Chamberlain's (p. 379) review of the transport of lead to man, he derives relationships for the uptake of lead from the major routes of intake, (inhalation and ingestion) and discusses results of experimental studies which utilize radioactive isotopes to verify the relationships for intake through the oral and inhalation routes, respectively. As well as using lead isotopes in experimental studies, Chamberlain refers to the use of ^{210}Pb, formed naturally in the atmosphere as a decay product of radon. Specific activity of ^{210}Pb in crops can be used to estimate the contribution of lead from fall-out to the diet and eventually to blood lead. However, Chamberlain indicates that when the relationship based on ^{210}Pb value is applied to individuals who live near highways or smelters, "rather frightening" estimates for blood lead result. He notes, however, that no such individuals have been described in Britain. Ter Haar (p. 339) criticizes the assumption that ^{210}Pb in food comes primarily from fall-out, and states that there is ^{210}Pb in soil which is not related to fall-out, to the extent that 90% of ^{210}Pb in food can be considered to be soil-derived. Ter Haar's value for dietary lead from fall-out is 1.3-1.6%, compared with 13-16% from the original study. Clearly the implications of this difference of interpretation need to be pursued.

In Chamberlain's summary of research recommendations, he proposes further investigation by duplicate diet studies to measure intake of lead from vegetables in areas of high lead fall-out, to complement existing data for areas of high soil lead from Britain and other parts of the world. He also recommends investigation of a possible pathway from lead in gasoline to the driver or passenger in a car, measurements of blood lead in venous blood (not capillary blood) from infants and mothers in areas of high environmental lead and, finally, more experiments on deposition of lead aerosol in the lung, particularly for particle sizes greater than 1 μm.

The workshop has provided us with a fairly comprehensive up-to-date review of not only the scientific literature but also the specific opinions of experts from a number of different disciplines and backgrounds. Agreement among experts was generally surprisingly good, but there are clearly several areas of controversy, which will be itemized and discussed in the final report.

2. GLOBAL LEAD CYCLE AND THE CANADIAN CONTRIBUTION TO IT

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Historical Aspects

Lead is believed to be the first metal to be won from its ores by mankind; man's discovery of the uses of lead occurred before 8000 BP (Nriagu, 1983a). Because of its softness, fusibility and lack of lustre, lead found limited application in weaponry, ornaments and jewellery, and hence remained the least glamorous of the metals of antiquity. Lead ores, however, are often married to silver, and, during ancient times, the mining of lead was very much a by-product of silver production, the lead mines being often referred to as silver mines. Indeed, most of the silver used in ancient times was derived from argentiferous lead ores using a process known as cupellation, discovered around 6000 BP (Nriagu, 1985a).

Lead nevertheless possesses unique properties that were to make it one of the most useful industrial metals of Greco-Roman times. During the first and second centuries AD, the production of lead stood at about 100,000 t a^{-1} (about 550 g per person per year), and the impressive level of consumption has led to lead being referred to as a 'Roman metal'. Lead production between 50 BC and 500 AD has been estimated to be about 15 x 10^6 (Table 1). The metallurgy of lead is extremely simple, and the rough-and-ready smelting techniques employed by the ancients were very wasteful, with up to 25% of the lead escaping into the air in the form of dense white fumes (Iles, 1904). The production and consumption of lead in ancient times thus resulted in very intense

Table 1.

Historical production of lead (from Nriagu, 1979, 1983b).

Period	Global Pb Production ($\times 10^6$ t)
3900-2100 BC (Copper Age)	3.2
2100-1200 BC (Bronze Age)	3.6
1200-50 BC (Iron Age)	14
50 BC - 500 AD (Roman Empire)	15
500-1000 AD (Barbaric Age)	4.2
1000-1850 AD (Renaissance, Middle Ages, etc.)	35
1850-1900 AD	25
1901-1910 AD	11
1911-1920 AD	11
1921-1930 AD	14
1931-1940 AD	15
1941-1950 AD	15
1951-1960 AD	24
1961-1970 AD	33
1971-1980 AD	38
TOTAL (all-time)	261

contamination of the local environment, and many ancient authors revealed that the region around the famous Greek lead/silver mines at Laurion was anathemical to health (see Nriagu, 1983a).

With the fall of the Roman Empire, mining in many parts of the world came to a virtual standstill. The Renaissance and the subsequent technological ascendance of western Europe must be attributed, in large measure, to the exploitation of the rich lead/silver mines of central Europe. The Industrial Revolution created a material culture with an insatiable appetite for metals. Lead mining became a world-wide pursuit, and the massive industrial installations used to extract and fabricate the lead were invariably equipped with tall stacks which broadcast the lead emissions very widely. Environmental lead pollution changed from being a local concern to being a regional and global problem. One of the most important commercial applications of lead, the use of lead alkyls as antiknock agents in gasoline, was discovered in 1923. With this application came the unrestrained spraying of large areas with biologically available forms of lead (NAS, 1980).

The historical trends in lead production are summarized in Table 1. Until the beginning of the last century, the tonnage of lead produced exceeded that of all other non-ferrous metals combined (Elliot et al., 1937). The all-time production figure is estimated to be 261 x 10^6 t, which is about 50% of the known lead reserves. The ancients consumed roughly 15% of all the lead so far produced, compared with the 62% that has been used since 1900. In fact, lead consumption during the past two decades alone constitutes almost 27% of all the lead that has ever been produced by mankind (see Table 1). Lead released into the environment closely parallels the trends in the historical production of this element.

The Global Lead Cycle

A phenomenological model of the global lead cycle can yield important insights into the recent human influence on the biogeochemical behaviour and rates of transfer of lead in environmental compartments. Such a model basically consists of a defined number of reservoirs or pools between which the transfer of lead occurs. The capacity of a given reservoir (or its burden) is derived as the product of the average lead concentration and the total mass of the medium in the reservoir. Table 2 summarizes the lead burdens in some of the principal reservoirs of the global lead cycle.

Table 2.

Inventory of lead in the earth's crust (compiled from the literature).

Reservoir	Total Mass (g)	Average Conc.	Pb Pool (g)
Lithosphere (down to 45 km)	$57x10^{24}$	16 µg g^{-1}	$9.1x10^{20}$
Sedimentary rocks			
Shale and clay	$1.8x10^{24}$	20 µg g^{-1}	$0.36x10^{20}$
Limestone	$0.35x10^{24}$	93.0 µg g^{-1}	$1.1x10^{18}$
Sandstone	$0.28x10^{24}$	1.5 µg g^{-1}	$0.42x10^{18}$
Soils (down to 100 cm)			
Soil organic matter	$6.8x10^{18}$	25 µg g^{-1}	$0.17x10^{15}$
Fossil fuel deposits			
Coal	$10x10^{18}$	10 µg g^{-1}	$1.0x10^{14}$
Oil shales	$46x10^{18}$	7.5 µg g^{-1}	$3.4x10^{14}$
Crude oil	$0.23x10^{18}$	0.05 µg g^{-1}	$1.2x10^{10}$
Terrestrial biomass			
Plants	$2.4x10^{18}$	0.1 µg g^{-1}	$24x10^{10}$
Animals	$2x10^{16}$	0.05 µg g^{-1}	$0.1x10^{10}$
Forest litter	$2.2x10^{18}$	1.5 µg g^{-1}	$3.3x10^{12}$
Oceans			
Dissolved	$14x10^{24}$	10 ng kg^{-1}	$1.4x10^{12}$
Consumers/producers	$3x10^{15}$	0.2 µg g^{-1}	$6.0x10^{8}$
Suspended particulates	$7.0x10^{16}$	0.6 µg g^{-1}	$4.2x10^{10}$
Pore water in sediments	$3.3x10^{23}$	0.3 µg kg^{-1}	$10x10^{13}$
Lakes and rivers	$3.4x10^{19}$	60 ng kg^{-1}	$2.0x10^{9}$
Freshwater biota	$3.3x10^{17}$	0.3 µg g^{-1}	$10x10^{10}$
Ground water	$4x10^{18}$	0.1 µg kg^{-1}	$4x10^{8}$
Glaciers	$2x10^{22}$	3 ng kg^{-1}	$6.0x10^{10}$
Atmosphere	$5x10^{21}$	3.5 ng kg^{-1}	$1.8x10^{10}$
Lead ore deposits			
Reserves	---	---	$1.4x10^{14}$
Resources	---	---	$1.5x10^{15}$

Most of the 9 x 10^{20} g of lead in the lithosphere resides in igneous rocks, and only a tiny fraction of it can be commercially recovered using present-day technology. The lead ore deposit reserve of 15 x 10^{14} g is about equal to the soil lead reservoir. The dissolved lead reservoir in the ocean is quite small, and hence can easily be influenced by large anthropogenic inputs (see below). In terms of 'environmentally available' lead, notice that the lead burden of fossil fuels exceeds the value for the known lead reserves.

The annual fluxes of lead along the major pathways of the global cycle are summarized in Table 3. Brief discussions of the cycling of lead in the individual 'spheres' follow, with emphasis on pathways and transfer rates that are most susceptible to human interference.

The Atmosphere

The world-wide emissions of lead from natural and anthropogenic sources are shown in Table 4. In recent years (1980), about 24,500 t lead are emitted annually from natural sources, a large fraction (65%) of which is derived from wind-blown dusts. This figure assumes that the dusts also contain technogenic lead, so that emissions in pre-technological times should have been much smaller. Patterson (1980) and Settle and Patterson (1980) gave considerably lower values for pre-historic emissions of lead from natural sources. Emissions from anthropogenic sources currently exceed contributions from natural sources by 14-fold. As most of the technogenic lead is emitted in the northern hemisphere (NAS, 1980), natural emissions in many parts of this region can be regarded as insignificant in relation to the man-made contributions. The principal sources of anthropogenic lead are gasoline and waste oil combustion (54%), other non-ferrous metal production (15%), lead production and consumption (12%) and iron and steel production (8.4%).

Table 3.

Fluxes of lead along the major pathways of the global cycle.

Pathway	Material Flux (g a^{-1})	Pb Conc.	Annual Pb Flux (g)
Atmosphere: Inputs			
Natural sources	---	---	$2.4x10^{10}$
Anthropogenic sources	---	---	$33x10^{10}$
Atmosphere: Outputs			
Deposition on land	---	---	$25x10^{10}$
Deposition into oceans	---	---	$11x10^{10}$
Oceans: Inputs			
Atmospheric fall-out	---	---	$11x10^{10}$
Waste discharges and storm runoff	$6x10^{19}$	1.0 µg kg^{-1}	$6x10^{10}$
Rivers, dissolved	$3.4x10^{19}$	60 ng kg^{-1}	$2x10^{9}$
Rivers, particulate	$1.5x10^{16}$	3.0 µg g^{-1}	$4.5x10^{10}$
Hydrothermal emanations	?	?	$1x10^{10}$
Oceans: Outputs			
Sea-salt sprays	$1.0x10^{15}$	2.4 µg kg^{-1}	$2.x10^{7}$
Sediments	?	?	?
Soils: Inputs			
Atmospheric fall-out	---	---	$25x10^{10}$
Fertilizer applications	$94x10^{12}$	10 µg g^{-1}	$9.4x10^{8}$
Waste disposal	$2x10^{12}$	30 µg g^{-1}	$0.6x10^{8}$
Litter fall	$2.2x10^{18}$	1.5 µg g^{-1}	$3.3x10^{12}$
Soils: Outputs			
Atmosphere	$5x10^{14}$	12 µg g^{-1}	$16x10^{9}$
Erosion (continental denudation)	$2x10^{16}$	12 µg g^{-1}	$24x10^{10}$
Biological assimilation			
Oceans	$6x10^{16}$	0. µg g^{-1}	$1.2x10^{10}$
Fresh waters	$1.0x10^{15}$	0.4 µg g^{-1}	$0.04x10^{10}$
Continents	$12x10^{16}$	0.15 µg g^{-1}	$1.8x10^{10}$

Table 4.

Natural and anthropogenic sources of lead emissions to the atmosphere (revised from Nriagu, 1979, 1985b).

Source	Emissions (10^9 g a^{-1}) Global	Emissions (10^9 g a^{-1}) Canada
Natural		
Wind-blown dusts	16	
Volcanogenic particles	6.4	
Vegetation	1.6	
Forest fires	0.5	
Sea-salt sprays	0.02	
Rock degassing	?	
TOTAL	24.5	
Anthropogenic		
Gasoline and waste oil combustion	177	8.4
Solid waste incineration	8.9	0.06
Coal combustion	15	0.02
Lead production	34	0.72
Industrial applications of lead	7.4	0.16
Non-ferrous metal production	50	1.0
Iron and steel production	28	0.02
Wood combustion	4.5	0.003
Miscellaneous	5.9	0.07
TOTAL	331	10
TOTAL EMISSIONS	355	

The total (all-time) quantity of anthropogenic lead that has been dispersed to the world ecosystems via the atmosphere is estimated to be 20 x 10^6 t (Nriagu, 1979). The steep historical change in rates of lead emission from anthropogenic sources since 1900 is depicted in Figure 1. As to be expected, about 40% of the total lead release has occurred during the past two decades. It should also be noted that the total lead emission is about 1000-fold higher than the amount of lead processed annually (1.8 x 10^{10} g) by terrestrial biota.

The mean residence time for lead in the present-day atmosphere of the northern hemisphere is given by:

$$Q/F = (0.5 \times 1.8 \times 10^{10}\ g)/(0.9 \times 33 \times 10^{10}\ g\ a^{-1}) = 10\ d$$

where Q is the atmospheric lead pool and F is the annual flux of lead into the atmosphere. The very rapid turnover rate (about 40 times per year) of lead in the air implies that long-term changes in emission intensity cannot always be reflected by corresponding changes in the ambient airborne lead levels. In other words, the concentration of lead in the atmosphere cannot be a good measure of the lead pollution burden in the environment. Assuming that the lead emitted in the northern hemisphere (30 x 10^{10} g a^{-1}) is uniformly distributed to a height of 10 km (hence volume = 2.5 x 10^{18} m^3), and using the estimated average residence time of 10 d, the average concentration of lead in the atmosphere is calculated to be about 3 ng m^{-3}. This figure actually agrees with the measurements at some remote locations in the northern hemisphere (Nriagu, 1978; Wiersma and Davidson, 1986). A similar calculation using emissions in pre-technological times suggests an average lead concentration of less than

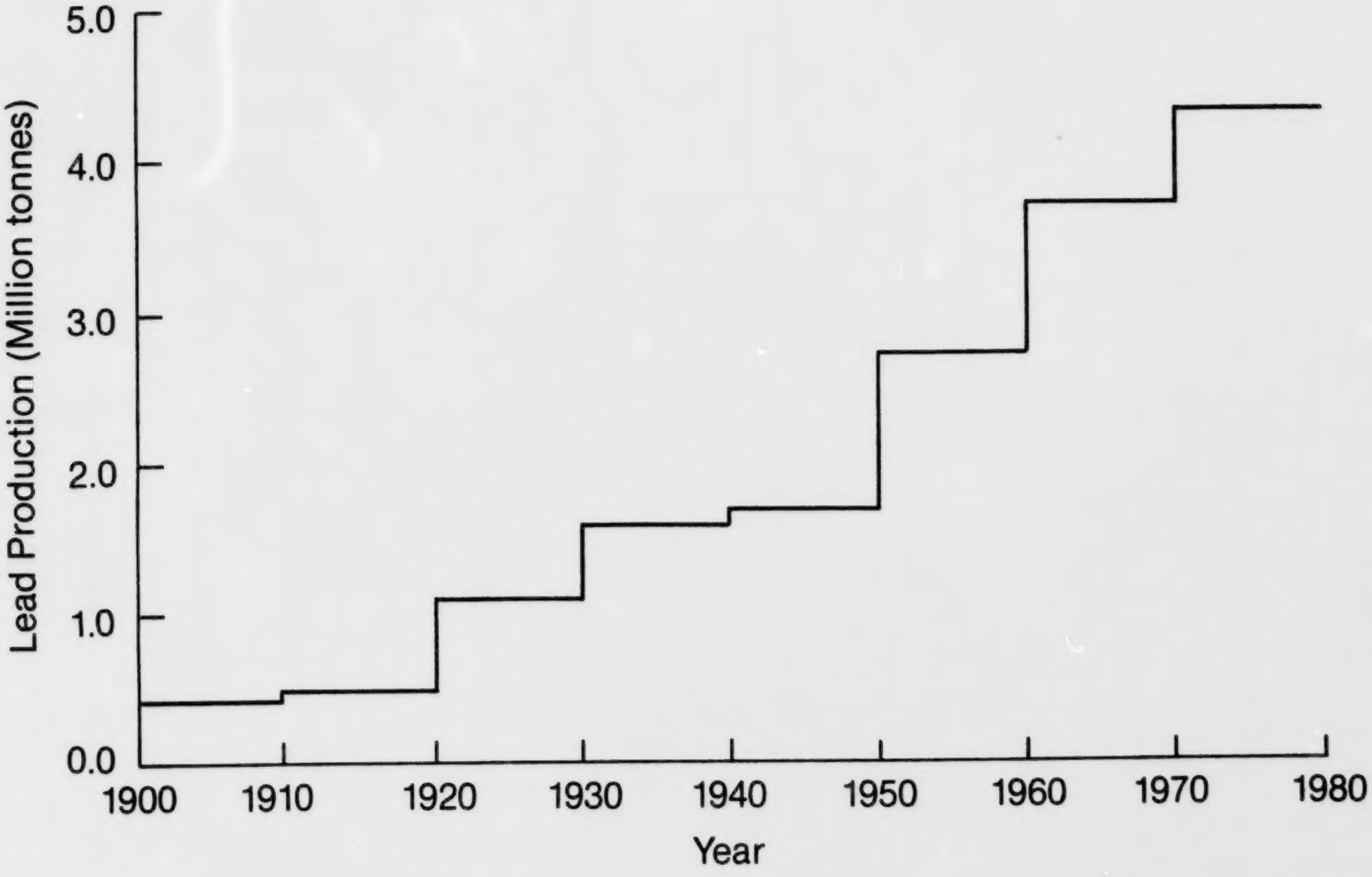

Figure 1. Historical trends in global emissions of lead to the atmosphere during the 20th century. (Data from Nriagu, 1979).

0.1 ng m^{-3}. Few places in the northern hemisphere still have such low ambient lead levels.

Much has been said about the human influence on lead in the atmosphere. This point is dramatically illustrated in Table 5, which shows the atmospheric deposition of lead at remote, rural and urban areas. The fall-out rate is the parameter believed to give a more realistic estimate of the intensity of lead pollution at a given location than the concentration in air. Accordingly, one is certainly left with the feeling that urban centres have become 'hot spots' of lead. As expected, the lead deposition in Greenland is about an order of magnitude higher than the measured rate in Antarctica (Boutron, 1985).

The Hydrosphere

The lead burden of fresh waters (1.2×10^9 g) is insignificant, even compared with that of the oceans (1.4×10^{12} g). This small reservoir, which is a critical life-support system for mankind, is, however, the one most heavily impacted by human activities. The lead in the freshwater reservoir is less than the atmospheric lead pool, and the impact of human activities upon it should be comparable if not more severe. For example, present-day lead concentrations in the Great Lakes are believed to be 10- to 90-fold higher than the levels in pre-colonial times (Nriagu, 1985b). Not much concern has so far been expressed about the pollution of surface waters with lead. Furthermore, studies of dated lake sediments suggest that the inputs of lead into lakes and rivers in many parts of Europe and North America have increased by up to 20-fold in recent times (MARC, 1985). Unfortunately, there are no reliable retrospective data to demonstrate whether there has been a corresponding increase in the lead content of the associated waters; it should, however, be noted that the half-life of lead in many lakes and rivers is very short (few

Table 5.

Atmospheric fallout of lead at remote, rural and contaminated areas (from NAS, 1980)

Site	Pb Deposition Flux ($mg\ m^{-2}\ a^{-1}$)
Near sources	
Toronto	6000
Missouri, 800 m from smelter	1265
Cincinnati, 10 m from highway	304
Toronto, near expressway	600
Urban	
New York City	350
New York City	547
Central Los Angeles	365-8000
Los Angeles Basin (Pasadena, California)	102-296
Los Angeles suburbs	17-120
San Diego, California	350
London, England	54
Madison, Wisconsin	25
Rural	
France (11 locations)	14.6
Northwest England	19.6
Walker Branch watershed, Tennessee	15.0
Delaware River watersheds	6.2
Mt. Moosilauke, New Hampshire	19.6
Upper Great Lakes Basin	12.0
Lake Michigan	15.0
Off Southern California coast	34.1
Remote	
Scandinavian glaciers	4.2
Sierra Nevada Mountains, California	4.0
French Congo	0.2
North-central Pacific Ocean	0.6
Eastern Pacific Ocean	0.09
North Atlantic Ocean	1.4
Northern Greenland	0.04
Greenland	0.08
Antarctica	0.01
North Atlantic Westerlies	1.7*
North Pacific Westerlies	0.5*
North Pacific Easterlies	0.06*
South Pacific Easterlies	0.03*

* From Settle and Patterson (1982).

days to few weeks), so that the buildup of lead in the water column should not be expected. It is also significant that the quantity of lead (4×10^8 g a^{-1}; Table 3) assimilated by freshwater biota represents only about 0.2% of the total lead burden; in other words, substantial anthropogenic inputs will drastically change the exposure commitment of the biota to lead.

The lead flux into the oceans comes mainly from the atmosphere (11×10^{10} g a^{-1}, or about 30% of total emissions), rivers (2×10^9 g a^{-1} dissolved, and 4.5×10^{10} g a^{-1} particulate), direct waste discharges and storm runoff from paved areas and buildings in coastal cities (6×10^{10} g a^{-1}), and hydrothermal emanations along the oceanic ridges (1.4×10^{10} g a^{-1}, but may be a lot higher). Chow and Patterson (1962) showed that about 99% of the lead entering the seas with the suspended load of rivers settles on the continental shelves and in the adjacent trenches and thus does not reach the pelagic areas. These estimates clearly suggest that the atmosphere is the principal supplier of lead to the open ocean, and recent studies have indeed demonstrated the strong influence of atmospheric pollution on the oceanic lead cycle (e.g. Burnett and Patterson, 1980; Schaule and Patterson, 1981; Settle and Patterson, 1982; Buat-Menard, 1984).

The domination of the oceanic cycle of technogenic lead is related to the fact that lead has a very fast cycle in the ocean, its residence time being only about 2 years in the surface waters and about 100 years in the deep ocean (Settle and Patterson, 1980). The strong atmospheric source has overwhelmed the steady-state oceanic cycle, resulting in lead concentrations in surface waters which are now always higher than levels in the deep waters. Such a profile for lead is unique and quite different from the steady-state profiles that have been reported for other trace metals in the ocean (Bruland, 1980; Bruland and Franks, 1983; Boyle and Huested, 1983; Burton et al., 1983). Furthermore, the magnitude of lead concentrations in oceanic waters is related to the rates of atmospheric input (Figure 2). The atmospheric depositions of lead in the North Atlantic Westerlies, North Pacific Westerlies, North Pacific Easterlies and South Pacific Easterlies have been reported to be 1.7, 0.5, 0.06 and 0.03 mg m^{-2} a^{-1}, respectively (Settle and Patterson, 1982). Correspondingly, the lead concentrations in surface waters of the North Atlantic are about 10 times higher than the levels in South Pacific surface waters (Settle and Patterson, 1982; Boyle and Huested, 1983; Bruland and Franks, 1983).

Soils

Atmospheric input of lead into the pedosphere (about 248,000 t a^{-1}) has had a marked effect on lead concentrations in soils on both local and regional scales. Assuming a background lead concentration of 12 μg g^{-1} and a soil density of 2 g cm^{-3}, a surface soil layer 1 m square and 1.0 cm deep would contain 240 mg of lead. The background atmospheric flux of 0.02-0.2 mg m^{-2} a^{-1} would correspond to an annual increase of about 0.007-0.07% of the original lead content, assuming that most of the lead stays in the top 1.0-cm soil layer. Since some of the dusts are re-entrained, it may be assumed that atmospheric inputs could not have significantly altered the pretechnological soil lead content. In rural areas, however, typical fluxes of 6-30 mg m^{-2} a^{-1} (Table 5) would represent annual increases of 2-10% of the lead in the top soil layer. A doubling of the soil lead content may be expected typically in 5-30 years, and elevated levels of lead have been documented in many rural soils (Nriagu, 1978). By contrast, the annual deposition rates of 200-600 mg m^{-2} a^{-1} in typical urban areas correspond roughly to the doubling of the soil lead content every 1-3 years. As expected, lead concentrations which are 1-4

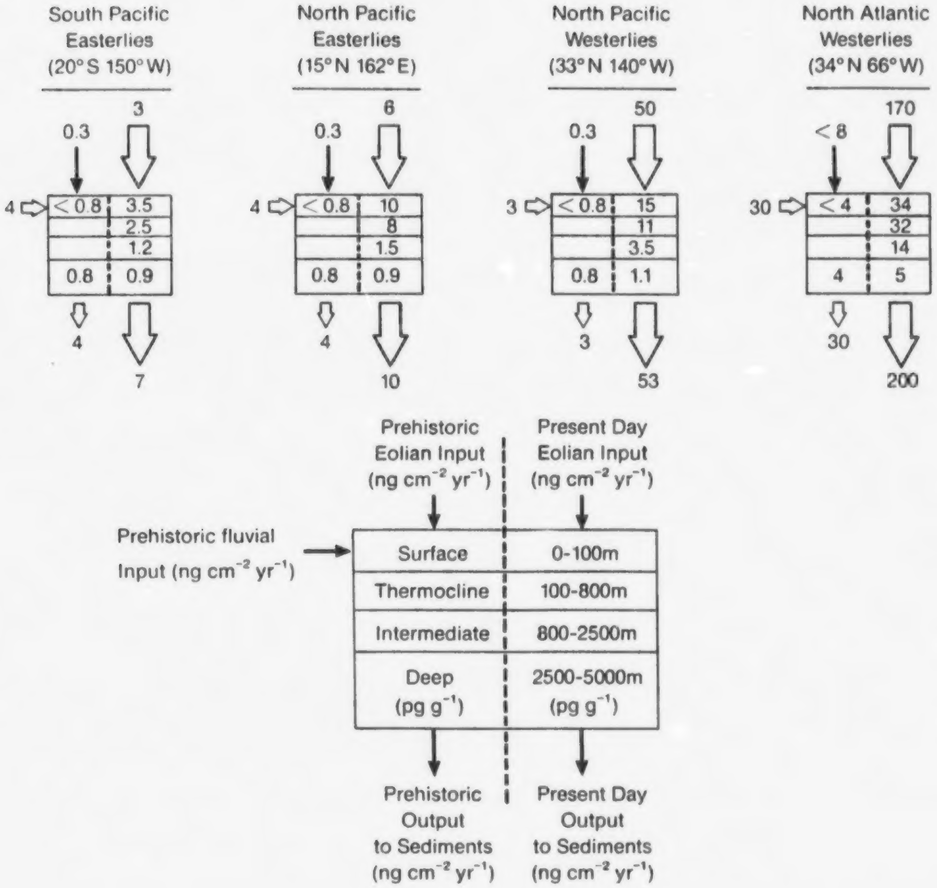
South Pacific
Easterlies
(20° S 150° W)
3
0.3
4
< 0.8
3.5
2.5
1.2
0.8
0.9
4
7
North Pacific
Easterlies
(15° N 162° E)
6
0.3
4
< 0.8
10
8
1.5
0.8
0.9
4
10
North Pacific
Westerlies
(33° N 140° W)
50
0.3
3
< 0.8
15
11
3.5
0.8
1.1
3
53
North Atlantic
Westerlies
(34° N 66° W)
170
< 8
30
< 4
34
32
14
4
5
30
200
Prehistoric
Eolian Input
(ng cm⁻² yr⁻¹)
Present Day
Eolian Input
(ng cm⁻² yr⁻¹)
Prehistoric fluvial
Input (ng cm⁻² yr⁻¹)
Surface
0-100m
Thermocline
100-800m
Intermediate
800-2500m
Deep
(pg g⁻¹)
2500-5000m
(pg g⁻¹)
Prehistoric
Output
to Sediments
(ng cm⁻² yr⁻¹)
Present Day
Output
to Sediments
(ng cm⁻² yr⁻¹)

Figure 2. Relationships between prehistoric and present-day atmospheric inputs, vertical concentration profiles and sediment outputs of lead in the oceans. (From Buat-Menard, 1984)

orders of magnitude above the background levels have become typical of many urban soils (Nriagu, 1978; NAS, 1980).

Other anthropogenic sources of lead in soils include fertilizer applications, waste (including slag) disposal and lead pesticide residues. These sources can have localized but potentially disastrous impacts on the soils and the crops grown on them (Thornton, 1980). The huge amount of litter produced per year carries with it a large amount of the immobilized lead (3.3×10^{12} g a^{-1}) to the soils where it may become permanently fixed into soil organic matter. It is estimated that 1.7×10^{14} g (or about 10%) of the lead in soils is bound to organic matter; it is a well-known fact that organic-rich soils generally contain more lead than soils depleted in organic matter.

Biota

Ultimately, all the lead produced and consumed by mankind is wasted in the biosphere. Thus, the biosphere now gains about 4×10^6 t lead annually at the expense of the lithospheric pool. The all-time gain of lead by the biosphere is estimated to be about 280×10^6 t (Table 1 plus the all-time emission figure). If all this lead were uniformly distributed among all the living things on land and seas, their lead content would increase 3000-fold. Of course, we know that most of the lead is biologically unavailable. Nevertheless, there is strong evidence to show that anthropogenic inputs now dominate many components of the biotic lead cycle.

As an example, the annual lead uptake by marine biota (1.2×10^{10} g a^{-1}) is now about 20-fold less than the annual anthropogenic inputs from the atmosphere alone. Whether the lead content of the biota in the open oceans has increased as a result is unresolved, but the Mussel Watch studies certainly point to spectacular elevations in biological accumulations of lead in the nearshore marine zones (see Eisler et al., 1978). Likewise, the annual assimilation of lead by terrestrial biota is about 14-fold less than the current atmospheric input, and the contamination of plants and vegetable crops with lead has become a matter of public health concern (Kloke et al., 1984). A case of note is the hardwood forest of New Hampshire, where the lead content of the forest biomass has increased at the rate of 23 g ha^{-1} a^{-1} between 1965 and 1977 (Smith and Siccama, 1981).

By consuming 1.2×10^{13} g of food plants (with average lead content of 0.1 μg g^{-1}) and 1.3×10^{15} g of animal biomass (lead content = 0.05 μg g^{-1}), mankind now ingests about 1.7×10^{7} g a^{-1}. This quantity of lead assimilated by man is insignificant compared with the amount used to maintain man's comfort and well-being.

Canadian Contribution to the Global Lead Cycle

The contamination of the Canadian environment with lead has been reviewed in another report by the Commission (Nriagu, 1985b). It was concluded that no place in Canada is free of lead pollution. The present-day atmospheric concentrations of lead in the most remote parts of the country exceed the pre-historic levels by up to 40-fold. At the present rate of lead release into the air, water and soils, even the rural areas of Canada will soon become over-contaminated with lead.

Emissions of lead to the atmosphere by industrial activities in Canada are compared with the global estimates in Table 4. It is seen that Canada contributes only 3% or so of the total lead released annually into the global atmosphere. Most of the lead, however, is released in a very small (inhabited) section of the country, and the contamination of urban areas in Canada is quite similar to the situation in most other countries. This point is emphasized by the atmospheric fall-out of lead in Canadian cities (Table 6). It needs to be stressed that these Canadian data are yearly averages; in view of the pronounced seasonality in reported fall-out rates, it would be erroneous to compare them with the results of synoptic measurements taken during only a few days and then extrapolated over the 1-year period. It must be noted, however, that very few lead fall-out measurements have been made in Canada. This must be considered a major oversight, since the fall-out rate best reflects the intensity of lead contamination of the environment.

Table 6.

Atmospheric lead fall-out in Canadian cities (1982) compared with deposition rates in the polar regions.

Location	Fall-out Rate (mg m^{-2} a^{-1})
Sydney, NS	310
Glace Bay, NS	73
Montreal	203
Toronto	339
Hamilton	555
Sault Ste. Marie	86
Thunder Bay	146
London, Ont.	129
Winnipeg	593
Greenland	0.029
Antarctica	0.004

The Great Lakes contain about 20% of the freshwater resources of the western world. Large inputs of lead into these lakes come from industrial operations in Canada. In this sense, Canada is contributing rather significantly to the world-wide contamination of fresh-waters with lead. Dated lake sediments also point to recent sharp increases in the flux of technogenic lead into lakes and rivers in many other parts of the country (see Evans and

Rigler, 1985).

Canada is a major producer and exporter of lead. Lead production exceeded 400,000 t a^{-1} in 1971, and has declined to about 300,000 t a^{-1} at the present time (Energy, Mines and Resources Canada, 1970-83). With time, most of this lead will be wasted in the environment and this means that Canada is now responsible for about 10% of the potential lead in the environment. By exporting two-thirds of all the lead produced, this country is in effect transferring the potential lead problem to other countries. Of course, most of the lead released during the mining and smelting of the lead ores stays in the Canadian environment.

Summary

Anthropogenic inputs now dominate the biogeochemical behaviour and rates of transfer of lead in many compartments of the global cycle, and Canada is a significant contributor of the lead which is being wasted in the biosphere. The observation is made that the atmosphere basically serves as a conveyor belt for lead, so that the lead fall-out rate should be regarded as a better measure of the environmental lead burden; few such data are currently available for locations in Canada. The freshwater lead reservoir or pool is tiny compared with the anthropogenic input, suggesting that the pollution of surface waters with lead may be more severe than has generally been realized.

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3. DISCUSSION OF CURRENT CAPABILITY FOR LEAD DETERMINATIONS, EMPHASIZING SPECIATION IN AIR

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Introduction

The elements can be grouped roughly into two categories: toxic and essential. A few elements do not fit easily into either category. Lead has been categorized as one of the 'toxic' group. It is also important to know how the toxicity of lead is affected by commonly associated elements, such as cadmium, sulphur, selenium, etc. In addition, it has become evident that the pathways of lead in the environment and its degree of toxicity depend very much on its chemical form (e.g. organic forms are more toxic than inorganic forms). This adds further difficulty to the assessment of the potential environmental and health hazards of lead and its compounds.

It would be reasonable to expect that the above problems could be addressed over a reasonable period of time if existing methods for the determination of lead and its compounds in environmental and clinical samples were capable of good precision and accuracy, or at least if the results were consistent among laboratories. Unfortunately, lead methodology, particularly in the case of lead compounds, has not yet reached the degree of accuracy and precision required for this purpose. Until recently there was abundant evidence that even 'total' lead data (when lead is extracted from samples by strong acid digestion or fusion and acid digestion) were not sufficiently precise and accurate for many purposes. An example of this from a 1975 clinical study (Lauwreys et al., 1975) is shown in Table 1.

Table 1.

Lead in clinical samples (from Lauwreys et al., 1975).

Sample	Units	n	Mean	Range	% of Labs with RSD* 10%
Blood C	µg dL^{-1}	51	15	3-49	47
D		52	24	10-87	65
E		55	23	1-115	--
Urine A	µg L^{-1}	33	63	5-159	42
B		34	84	8-185	47
Aqueous solution 1	µg L^{-1}	51	209	25-670	65
2**		50	194	18-580	--

* RSD = relative standard deviation.
**Dilution by 10 of aqueous solution 1.

In addition to this study, I can demonstrate from personal experience the inadequacy of lead data at least up until about 1980. An example of this is a lead laboratory intercomparison study for the analysis of environmental samples in which my laboratory was involved (Morrison, 1979). Data from this study are given in Table 2. Data from a recent study of the determination of lead in blood in which my laboratory is still participating (1984 to the present) show that all 16 laboratories obtain acceptable results 68-100% of the time.

In addition to the uncertainties demonstrated in much of the above, there is another aspect of most laboratory operations which implies that the reliability of lead data until quite recently (and in many cases still) cannot be known. This is the lack of a valid and comprehensive quality assurance

Table 2.

Lead in water sludge and sediment: interlaboratory comparison (from Morrison, 1979).

	Water* ($\mu g\ L^{-1}$)			Sludge	Sediment ($\mu g\ g^{-1}$)	
Parameter	1	2	3	($\mu g\ g^{-1}$)	1	2
Mean of labs	6	4	334	1690	14	14
Standard deviation	4	3	56	120	5	6
Range	2-130	2-170	280-420	1-2500**	5-20	4-25

* Water 1 and 2 are splits of same sample.
**One lab used H_2SO_4, thus precipitating most lead.

programme in most laboratories. It has been falsely assumed by many that successful performance in interlaboratory comparison studies is sufficient to validate their data. However, it is abundantly clear that sampling (including choice and use of samplers and containers), storage and physical sample preparation (not usually a part of interlaboratory comparison studies) are commonly the greatest sources of error in a determination. Thus it is absolutely essential that comprehensive quality assurance programmes, such as those described by King (1982), be established immediately in all chemical analysis laboratories.

As if the above shortcomings were not enough, a further problem with lead data is the establishment of valid background or 'normal' values. An interesting history of chromium values reported for blood was compiled by Mertz (1975). He demonstrated that over the period 1948-74 the values obtained for 'normal' blood varied by up to 3 orders of magnitude, and that a trend to lower values occurred in recent times. Such a problem (perhaps of differing magnitude) would also be demonstrable for lead. The recent trend to lower levels in blood may be due in part to methodological improvements and better instrumental detection limits. Major factors which inhibit an unequivocable agreement in 'normal' or background values are lack of sensitivity, poor interference correction (particularly background correction) and contamination. In the case of contamination, in my laboratory we were unable to determine lead at the submicrogram per litre level 3 years ago because our blanks showed a pick-up of lead from reagents, dust and air such that the blank values were above 0.5 μg L^{-1}. Table 3 is included to compare detectable amounts (3x detection limit under best conditions) by different analytical methods.

Table 3.

Detectable amounts of lead by various techniques.

Technique	Pb Detectable Amount (μg L^{-1})
Anodic stripping	0.01
Flame atomic absorption	60
Furnace atomic absorption	0.03
Inductively coupled plasma emission	40
Inductively coupled plasma mass spectrometry	0.15
Neutron activation	500

Speciation

With this background I will very cautiously introduce the idea that considerable strides are now being made in developing methodology for the determination of the chemical forms of lead in natural samples. Remember that all the above discussions of analytical uncertainty were related to total lead values, an analysis which should be considerably easier than the determination of chemical forms of lead. It is important to emphasize that the levels of the chemical forms should sum together to equal the 'total' lead value. This means, of course, if we are having difficulty obtaining 'total' lead levels (as we do particularly near background), then we will surely have an even greater challenge in breaking that value down to evaluate the level of its chemical components.

Determination of the chemical form (speciation) of lead can be achieved by a number of procedures depending upon sample type, the species to be determined and the levels of lead present. When discrete lead compounds are to be determined, electrochemistry or chromatographic methods are most commonly employed. In theory, electrochemical methods should be an excellent approach to lead speciation. Lead is one of four metals which inherently give excellent detection limits. However, using electrochemical methods in complex, real-sample solutions such as generally encountered in lead work presents severe difficulties (or perhaps difficulties beyond my capabilities). Chromatographic methods, on the other hand, work well in complex matrices. The one serious shortcoming of such methodology, however, is that it cannot be utilized with labile compounds.

A number of laboratories around the world (and this number is increasing greatly at present) have been using the many techniques of chromatography combined with atomic spectrometry detectors for lead speciation work. Atomic spectrometry detectors include flame and furnace atomic absorption (AAS), inductively coupled plasma (ICP) and microwave-induced plasma (MIP) emission, mass spectrometry, ICP source mass spectrometry and flame and furnace atomic fluorescence (Van Loon et al., 1977). The advantage of atomic spectrometry detectors over commercially available conventional detectors is that they are metal-specific. Because of this, the chromatogram produced contains peaks only of the compounds of the element(s) of interest. Work of this type is relatively easy compared with similar work with conventional detectors. A useful critical discussion of instrument configuration, interface types and methodologies can be found in a recent review (Van Loon, 1983).

Lead Speciation in Air

My colleague, Dr. Y.K. Chau, at Canada Centre for Inland Waters has been a pioneer in lead speciation work. We have been fortunate in having his involvement in our work on determining lead species in air (Radziuk et al., 1979). Dr. Chau has also done some excellent work on lead speciation in a variety of other samples being discussed in this paper. Of particular note is Chau's methodology for the important trialkylleads and related compounds, substances which we have not thus far determined. Because Dr. Chau is also presenting a paper here, I will restrict my discussions to work other than that by Chau, referring to his research only when it overlaps with ours.

The following is not meant to cover all the procedures for lead species in air but is representative of the major approaches now being employed.

Lead Speciation in General

A variety of lead species have been identified in the environment. The main ones are inorganic lead, tetraalkylleads, trialkylleads and dialkylleads. These compounds have been detected or postulated in air, water, sediment and biological species. Figure 1 is a biogeochemical cycle for tetraalkylleads as postulated by De Jonghe and Adams (1982). This reference is a review of measurements of organic lead in air, and can be consulted for further details.

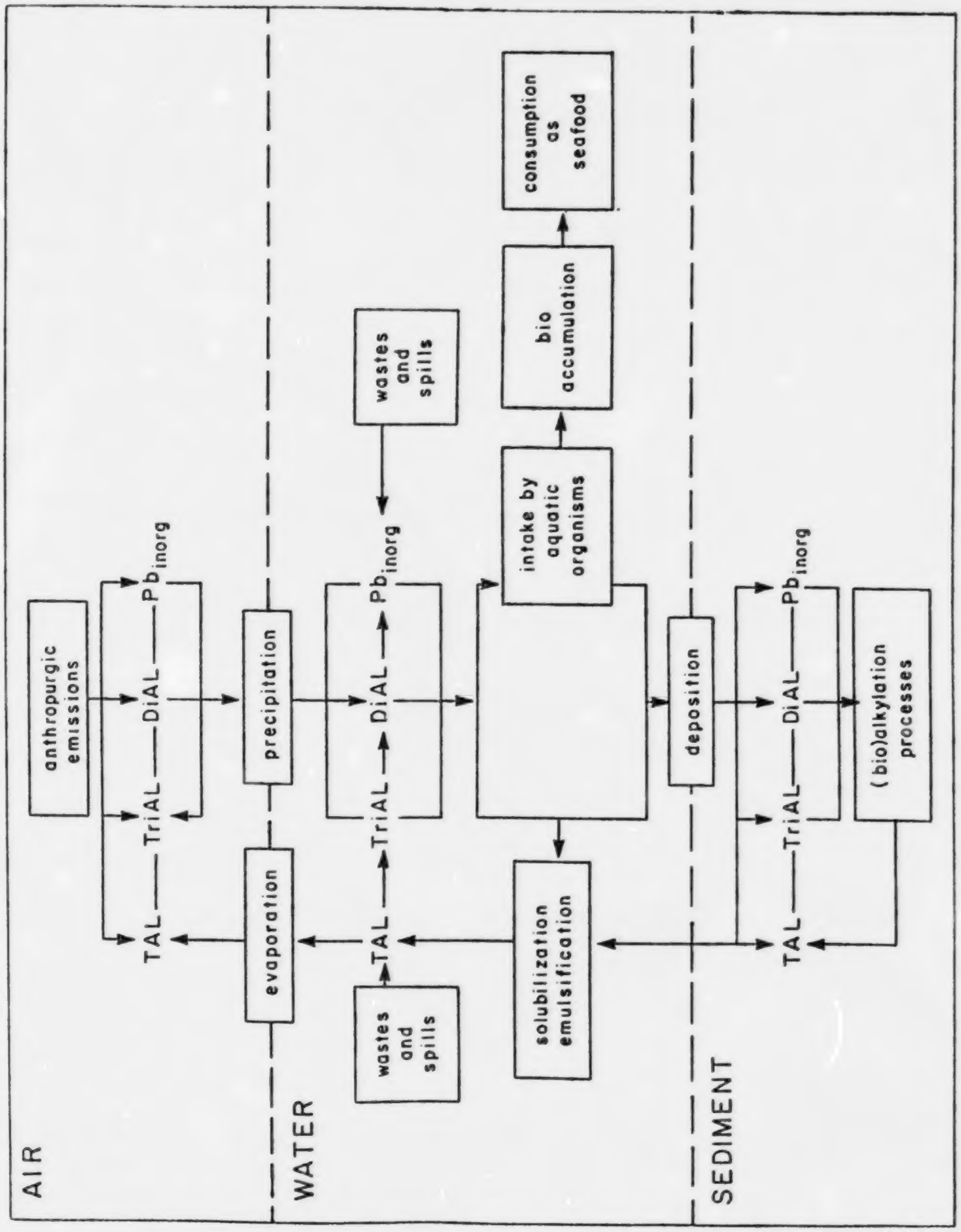
AIR
WATER
SEDIMENT
anthropurgic emissions
TAL
TriAL
DiAL
Pb inorg
evaporation
precipitation
wastes and spills
TAL
TriAL
DiAL
Pb inorg
wastes and spills
solubilization emulsification
intake by aquatic organisms
bio accumulation
consumption as seafood
deposition
TAL
TriAL
DiAL
Pb inorg
(bio)alkylation processes

Figure 1. Biogeochemical Cycle for Tetraalkylleads. From D. Jonghe and Admas (1982).

Procedures for the determination of lead species in air fall into two broad subdivisions. Following filtration (usually through membrane filters of 0.45-μm porosity) methods are for (i) the particulates, and (ii) the non-filterable fraction. In most cases it is assumed that the particulate fraction contains only inorganic lead, an assumption which is incorrect in most cases (trialkylleads and dialkylleads can exist in residues). The non-filterable fraction consists of organolead vapours.

De Jonghe and Adams (1982) distinguished between three different types of methodologies. These are (i) methods which yield data on the total amounts of organic lead of the non-filterable fraction (the term 'total' organic lead should be avoided since some may also be trapped in residues), (ii) methodology which determines the volatile lead compounds termed 'volatile organic lead', and (iii) speciation methodology which gives concentrations of the individual tetraalkylleads. It is particularly difficult to relate and distinguish between (i) and (ii). There is also great difficulty at this stage in comparing results for the same substance obtained by different methodologies. I shall give particular emphasis to category (iii), which gives information on the actual concentrations of the individual tetraalkyllead compounds in air. It has been found that tetraethyllead is significantly more toxic than tetramethyllead (Cremer and Callaway, 1959).

Determination of 'Total' Organic Lead and Volatile Organic Lead

Although the term 'total' organic lead should be avoided, as noted above, its use pervades the literature, and a relatively large number of procedures exist for its determination. All useful methods involve a collection/concentration step. Approaches are as follows:

1) Reactions with iodine, e.g. vapours of organic lead are passed

through iodine crystals or iodine solutions to form lead iodide salts which are non-volatile (Cholak, 1962).

2) Reactions with iodine monochloride (Hancock and Slater, 1975) in which tetraalkyllead compounds are trapped as dialkyllead salts. Inorganic lead is masked with EDTA and organic solvent.

3) Absorption of organic lead on activated charcoal. The most successful procedure using this approach involves treatment of the activated charcoal to form an iodized coating. This improves the collection efficiency (Birnie and Noden, 1980). Lead thus collected is commonly determined by atomic absorption.

Values for 'total' organic lead obtained by all these approaches are probably too low because of failure to include any appreciable trialkyllead and dialkyllead which remain in large part with the filterable fraction.

For volatile organic lead, cold trapping is usually employed. Short lengths of packed gas chromatogaphic (GC) column are typically used as the trapping medium (Harrison et al., 1974). In order to obtain a better pumping flow rate, glass or polymer spheres have also been employed (Jang et al., 1981). The latter was less susceptible to clogging (due to the co-deposition of ice from the moisture in the air). A separate pre-moisture trap can also be used, but any volatile lead compounds must be subsequently removed from this onto the volatile lead trap. The volatile lead thus collected is released by warming, and is usually determined by atomic absorption spectrometry.

Determination of Tetraalkylleads by Liquid Chromatography

Relatively little lead high-performance liquid chromatography (HPLC) has been reported. This is because of the rather poor detection limits recorded to date by this approach. The most common application is the liquid chromatographic determination of individual tetraalkyllead compounds in gasoline (Ruo et al., 1977; Brinkman et al., 1977; Ibrahim et al., 1984). Levels in gasoline are high enough to be determined in this way. In the paper by Brinkman et al., (1977), detection limits of 42 ppb tetramethyllead and 212 ppb tetraethyllead were reported for HPLC with ICP detection.

Levels of lead species in gasoline are very relevant to levels in air. Liquid chromatography has the following inherent important advantages over gas chromatography. It can separate thermally unstable and high-molecular-weight compounds. For this reason it would be important to develop further this line of research. In this regard better detection limits would be achievable if after the HPLC separation the lead compounds were destroyed and the lead methylated and swept in the gas phase into a flameless AAS or MIP emission detector.

Determination of Individual Tetraalkylleads by Gas Chromatography

Of the total work done on metal organic compounds by gas chromatography (GC)/atomic spectrometry, lead speciation is second only in number of procedures to mercury compound determinations. Thus at this date there are some relatively sophisticated methods for the determination of individual tetraalkylleads in air.

There is a considerable body of literature on the determination of tetraalkyllead compounds in air by GC using conventional detectors such as the electron capture detector (Cantoni and Cantoni, 1968). Gas chromatographic methods usually employ a short piece of packed GC or glass sphere column as a trap, much as these are used for volatile lead determinations. The compounds thus trapped are evolved by heating onto the main gas chromatographic column for separation.

Laveskog (1970) applied gas chromatography/mass spectrometry to the determination of tetraalkylleads in street air. In his work a cooled (-80°C), short, packed GC column was employed as a collection trap. He used a medium resolution mass spectrometer and obtained results much higher than subsequent workers (perhaps due to serious undetected interference problems).

A number of researchers have employed gas chromatography with atomic absorption or atomic emission detection of tetraalkyllead compounds. Again the compounds were trapped on cooled, short, packed pieces of GC column (Radziuk et al., 1979) or on cooled glass sphere traps (De Jonghe et al., 1986) which give improved sample flow rates. The compounds thus trapped were evolved by heating onto the main gas chromatographic column for separation. Together with the trapped tetraalkyllead compounds will be a large variety of other organic compounds not containing lead but which co-elute with the tetraalkylleads. However, because atomic absorption and atomic emission detectors are element-specific, the chromatographs will consist solely of lead compound peaks. Using short, packed GC column traps (which require relatively long sampling periods and low flow rate), Radziuk et al. (1979) using atomic absorption furnace detector and Reamer et al. (1978) using microwave-induced plasma emission detection both achieved 0.5 ng m^{-3} detection limits for individual tetraalkylleads in air based on 16- and 2-h sampling times, respectively. De Jonghe et al. (1986), using a cooled glass sphere trap, used a 1-h sampling time and achieved 0.2 ng m^{-3} detection limits. It would be of great interest to use the De Jonghe et al. (1986) glass sphere trap together with the Reamer et al. (1978) microwave-induced plasma emission detector which would in theory give the best detection limits.

Concentration of Lead Species in Air Samples

Values for total organic lead reported in the literature measured in large USA and European cities range from 0.5 to over 100 ng m^{-3} for adjacent rural/residential locations and up to 2000 ng m^{-3} for urban high-traffic-density locations. Available data on volatile organic lead values are relatively few, and range from 3 up to 1000 ng m^{-3} for high-density urban locations. Tetraalkyllead compounds as individual components have been measured in the air of USA, Canadian and European cities. Adjacent rural/ residential sites have concentrations which range from 0.5 to 60 ng m^{-3}, depending on the compound. High-traffic sites have concentrations ranging up to 400 ng m^{-3}. The only Canadian values found in the literature to date are those from my group (Radziuk et al., 1979) for Toronto. A typical urban air sample collected at College and University Avenues in 1979 contained concentrations of 0.5, 1, 1, 2 and 8 ng m^{-3} for tetramethyl-, trimethylethyl-, dimethyldiethyl-, methyltriethyl- and tetraethylleads, respectively. The presence of organolead compounds other than tetraethyllead in Toronto air is surprising, considering that only tetraethyllead was added to gasoline in Ontario at that time. This may be due to exchange of methyl and ethyl groups, a reaction which appears to be photolytic in nature. The presence of tetraalkyllead compounds in urban air seems to be mainly due to evaporation of gasoline. Combustion of these compounds to inorganic lead is relatively complete in motor vehicles.

Distinguishing Between Anthropogenic and Natural Lead Sources and Source Identification

At present there is a paucity of reliable information on this topic. I see a very good opportunity for direct measurements in this subject area using the very recently introduced approach of inductively coupled plasma source mass spectrometry. An excellent review of this technique has been recently published by Douglas and Houk (1985). Inductively coupled plasma source mass spectrometry yields detection limits in the low to subnanogram program range. This approach can be used for conventional trace element analysis. In addition, isotopic ratio determinations can be made. Because lead isotopic ratios are typically characteristic for a given source or ore deposit, it would in theory be possible to measure lead isotopic ratios for lead species in the field and relate these back to lead ore sources. Another important contribution of the technique is that isotope dilution mass spectrometry (the method against which most other methodology is compared) can be done relatively readily. I feel very optimistic for future lead work. My laboratory is, together with Professor J.B. French's Aerospace Studies at the University of Toronto, beginning studies of environmental lead using inductively coupled plasma mass spectrometry.

Top Research Priorities in this Field

These are as follows (not in any order):

1) Development of methodology with better detection limits. (It is crucial that we be able to establish 'true' background levels.)

2) Establishment of valid and comprehensive quality assurance programmes in all laboratories doing trace lead determinations. (It is crucial that we obtain valid assessments of accuracy and do valid interlaboratory comparisons.) Development of inductively coupled plasma source mass spectrometry for isotope dilution mass spectrometry determinations is an important aspect of accuracy assessment.

3) Development of chemical analysis methodology which is simultaneous multi-element in character. (This will allow co-determination of important coexisting elements with lead.)

4) Improvement of capability to determine individual lead species. This involves developing methodology with improved detection limits and high specificity. In this regard I suggest an emphasis on the use of microwave-induced plasma emission spectrometry with gas chromatography.

5) Development of a capability to do lead isotopic ratios relatively simply and rapidly. (This will be an important tool for source identification.) The best approach appears to be inductively coupled plasma mass spectrometry.

6) Development in Canada of specimen banking facilities and programmes. This is a newly developing field which is being pioneered in Germany and the USA. Such programmes are essential to allowing the analysis of today's samples in the future when chemical analysis technology is vastly improved. It will allow the future establishment of valid data for samples which have generally lower lead levels. Also in the future, as new parameters are discovered which may give important new dimensions to lead studies, it will be possible to retrospectively analyse today's samples (Lewis et al., 1985).

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4. LEAD IN THE ATMOSPHERE: CONCENTRATIONS, SIZE DISTRIBUTIONS AND DEPOSITION

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Introduction

Of all trace elements in the environment, lead has been the most widely studied. Recent summaries of the literature indicate that several thousand journal articles have been published on this element in the past two decades (EPA, 1985). Although the amount of lead research has decreased somewhat since 1980, several hundred articles are still being added to the information base each year (Davidson, 1982).

Much of the research involving environmental lead has focussed on the atmosphere, the single most important reservoir for anthropogenic lead emissions. Nriagu (1978) estimated that 460,000 t lead were emitted to the atmosphere each year during the mid-1970s. Of this amount, approximately 95-99% was due to anthropogenic activities, whereas only a few per cent at most was natural (Nriagu, 1978; Patterson, 1980). Total anthropogenic emissions are smaller today than during the 1970s because of decreasing lead in gasoline, but natural emissions are still a small fraction of the total. It is clear that man's activities have greatly perturbed the natural distribution of lead in the atmosphere, making this an important topic of study.

This paper briefly summarizes current knowledge on lead in the atmosphere. Firstly, airborne lead concentrations in urban, rural and remote areas are presented. Issues concerning reliability of these data are also discussed. Secondly, size distributions of atmospheric lead are summarized. This section includes individual distributions reported in separate investigations as well as averages according to sampling site category: urban, non-urban continental and marine sites. Finally, the use of the size distribution data to predict deposition in the human respiratory tract and dry deposition onto natural surfaces is discussed.

Airborne Concentrations of Lead

Table 1 provides data on airborne lead for urban and rural areas as summarized by Nriagu (1978). Overall, the data show that lead levels in urban areas are typically 1-10 $\mu g\ m^{-3}$, whereas those in rural areas are often 0.1-1 $\mu g\ m^{-3}$. Several locations report values outside these ranges, however. Note that several concentrations are given for Canadian cities, provided by the National Air Pollution Surveillance (NAPS) Reports of the Air Pollution Control Directorate in Ottawa. In general, the concentrations at sites in Canada are in reasonable agreement with other urban and rural locations worldwide. Concentrations in urban and rural areas today may be somewhat lower than these values, however, because of decreasing emissions from combustion of leaded gasoline.

Lead concentrations in remote areas are summarized in Table 2, after Wiersma and Davidson (1986). The values range from less than 0.001 to 0.1 $\mu g\ m^{-3}$. Many of the concentrations are less than 0.01 $\mu g\ m^{-3}$, particularly those measured in remote arctic, antarctic and oceanic locations. In comparison with the data in Table 2, the concentrations in Table 1 have been elevated significantly above natural background levels due to anthropogenic activities in urban and rural areas.

It is of interest to consider the reliability of the data summarized in these tables. When the concentrations in Table 1 are plotted as a function of sampling year, the scatter plot shown in Figure 1 is obtained. A best-fit polynomial curve is shown on the graph. Note that there is a steady decrease in average lead concentration throughout the time period. Several factors might be responsible for this decrease, such as improvements in sampling and analytical techniques, differences in sampling location from year to year and overall real decreases in airborne lead. The importance of the last factor can be assessed by examining National Air Surveillance Network (NASN) data (EPA, 1980). The overall average concentrations for each year for several NASN urban sampling sites throughout the US are shown in Figure 2. Relatively constant concentrations prior to 1977 suggest that the true airborne lead levels represented in Figure 1 were not decreasing with time during most of the 25-year period shown. There are no significant changes with time in the fractions of rural and urban sites in Table 1, suggesting that the decreasing trend in Figure 1 is not due to shifts in sampling sites to more rural areas. It is thus probable that the apparent trend in Figure 1 reflects improvements in sampling and analytical techniques, particularly in controlling contamination, improving detection limits and correcting for interferences.

The same conclusion may be reached by comparing the data in Table 2 with earlier literature reviews concerning remote areas. Rahn (1976) summarized concentrations of lead in remote areas of the world from sampling efforts during the 1960s and early 1970s. A similar review of remote area lead levels was conducted by Nriagu (1978). Both reviews reported few concentrations less than 1 ng m^{-3}. In contrast, the data in Table 2 include several concentrations as low as 0.1-0.2 ng m^{-3}. The implication of Tables 1 and 2 is that urban, rural and remote region airborne lead data prior to the 1970s are more

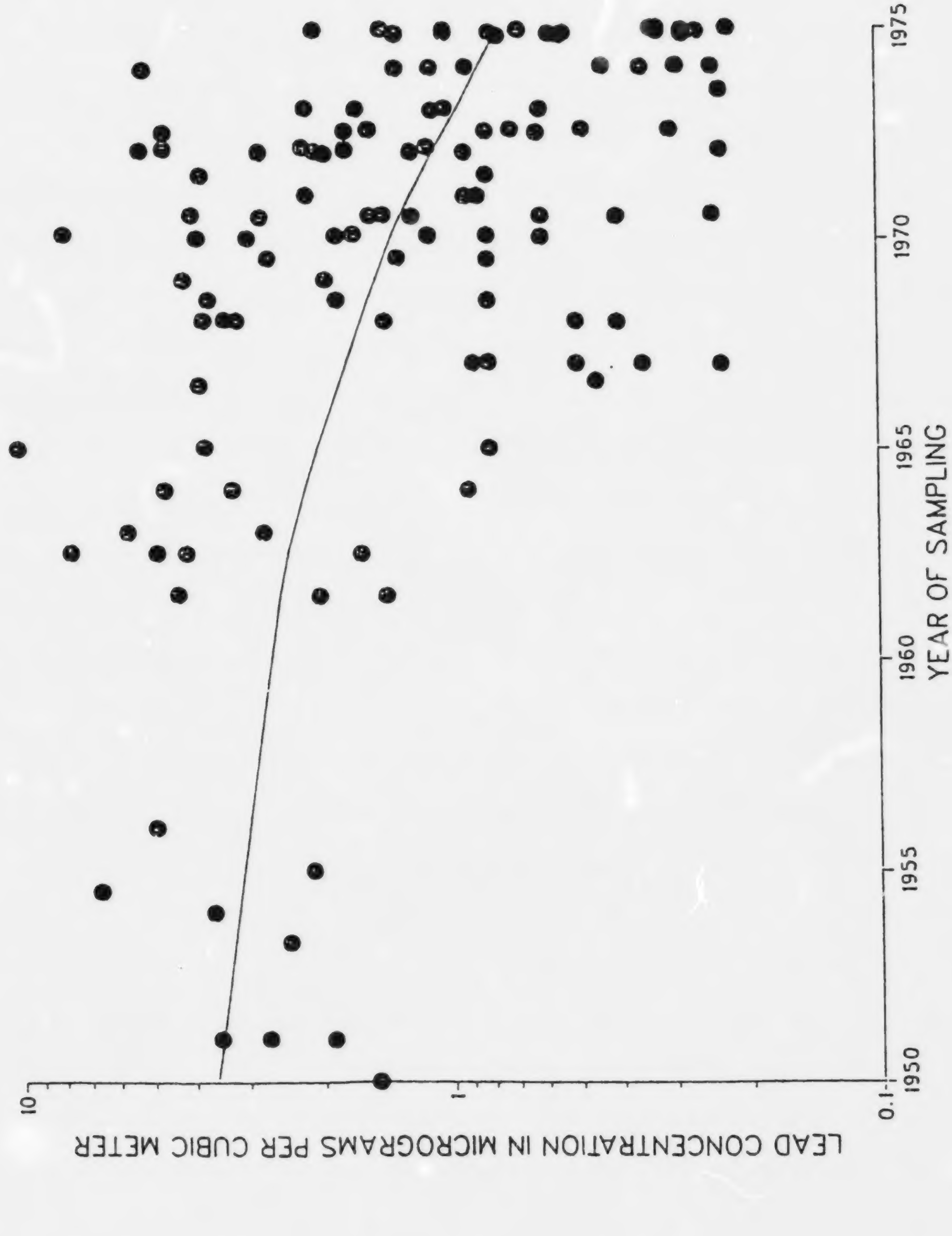

Figure 1. Urban Airborne Lead Concentration Versus Year

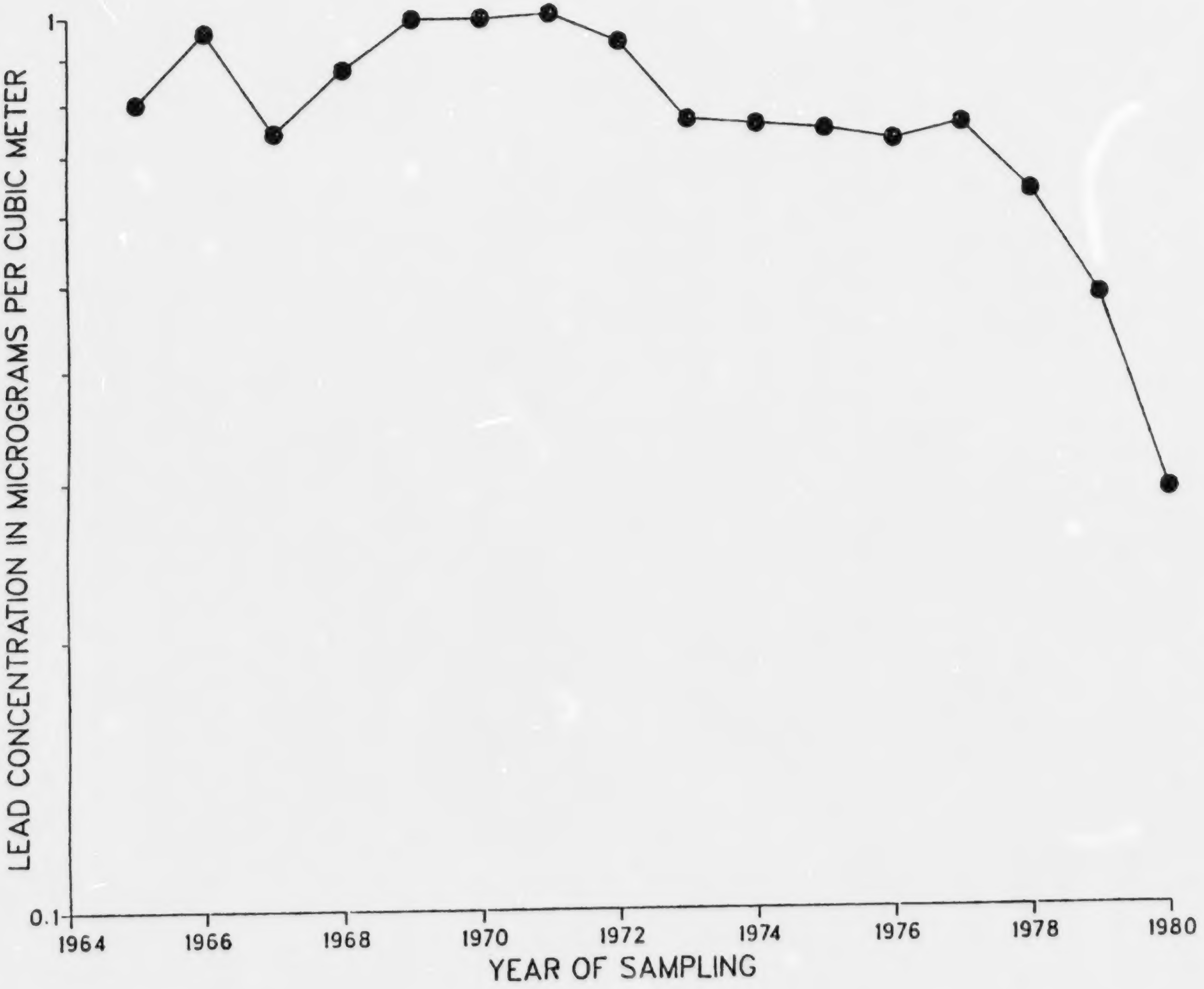

Figure 2. Urban Airborne Lead Concentration Versus Year EPA NASN and NAFN Data.

likely to be erroneous than recent data. The problem is probably more serious in areas of very low lead concentrations, where recent data may also be suspect (Patterson and Settle, 1976; Boutron and Patterson, 1983).

Size Distributions of Airborne Lead

The data of the previous section were obtained, in most cases, with filters which capture particles of a wide range of sizes with high efficiency. The values reported in Tables 1 and 2 thus represent total airborne concentrations of lead associated with most particle sizes. In a more limited number of studies, investigators have fractionated airborne particles by size before subjecting the samples to chemical analysis.

Several such studies have been reported in the literature for lead. Examples of these distributions are shown in Figure 3 (Davidson and Osborn, 1985). The ordinate of each graph is the normalized mass distribution function:

$$(\Delta C/C_T)/\,\Delta \log d_p \qquad (1)$$

where ΔC = airborne mass concentration of lead in a given size range (which extends from $d_{p\ min}$ to $d_{p\ max}$)

C_T = total concentration of lead in all size ranges

$\Delta \log d_p = \log d_{p\ max} - \log d_{p\ min}$

The aerodynamic diameter of a particle d_p represents the size of a unit density sphere whose aerodynamic transport characteristics are identical to those of the original particle. Note that the area under the curve between any two particle diameters is proportional to the fraction of airborne mass in that size interval. Data to construct these graphs have been obtained from differential or cumulative distribution plots, or from tables, in the original references. Personal communication with the authors was necessary in several instances to clarify or update the data.

All distributions have been plotted as though the particles are uniformly distributed in log d_p in each size range. The resulting histograms are thus only approximations to the true smooth-curve distributions which are unknown, although techniques for estimating the true size spectra have been reported in the literature (Esmen, 1977; Raabe, 1978). For consistency, overall minimum and maximum aerodynamic diameters of 0.05 and 25 μm, respectively, have been assumed after Hidy (1974) and Davidson (1977), except for a few cases where investigators have taken special measures to characterize distribution end-points. This style of graphing has been chosen to allow direct observation of those size ranges containing the bulk of the airborne mass, and to emphasize differences in the shapes of the distributions. Such differences would be more difficult to identify in cumulative log probability plots. Pertinent data associated with each of the graphs are given in Table 3. Listed in the table are the authors, dates of sampling, location and type of equipment used in each study.

Overall, the plots indicate that lead is predominantly in submicrometre particles. Except for the few distributions obtained without backup filters (numbers 9, 14, 17, 18 and 37 in Figure 3), most of the lead mass is associated with the lower end of the spectrum in each case. This has important implications for the transport of atmospheric lead: small particles are slow to deposit onto natural surfaces, and hence may remain airborne for long periods of time. Distances of transport are thus likely to be large.

Figure 4 shows averages of several lead size distributions by sampling location, after Milford and Davidson (1985). These averages were computed using 41 size distributions reported in the literature. The distributions in-

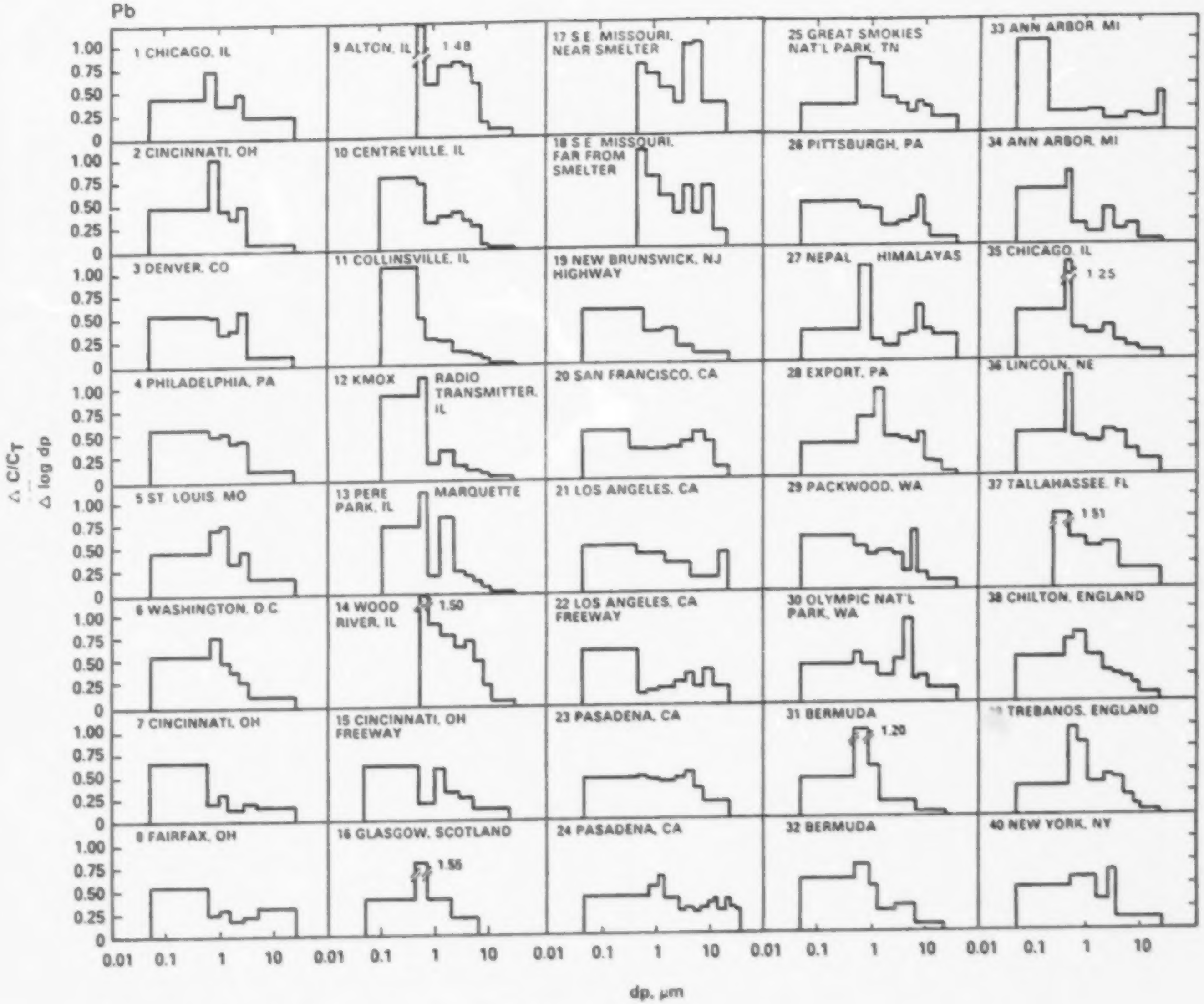

Figure 3. Size Distributions of Airborne Lead.

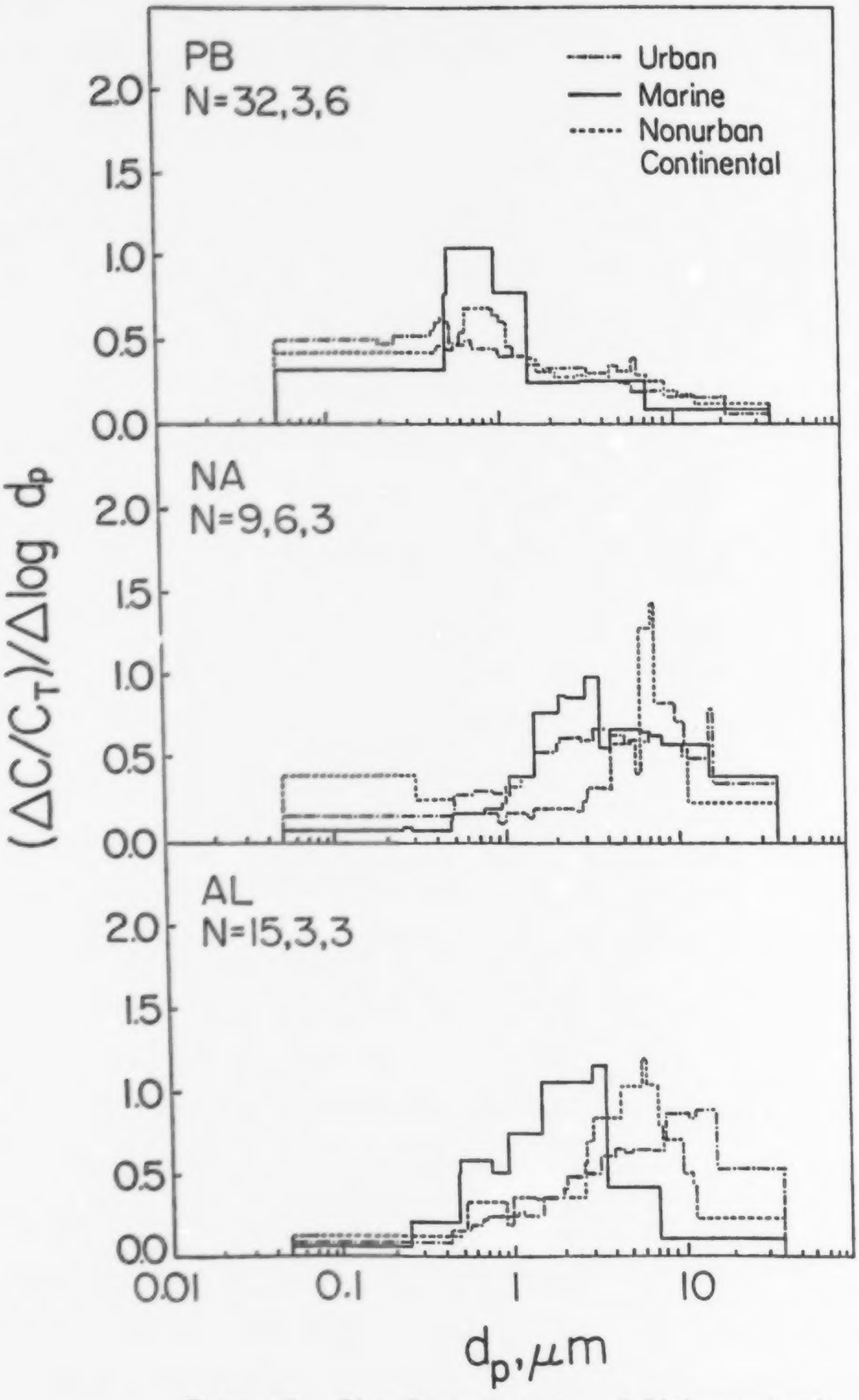

Figure 4. Size Distributions of Airborne Lead.

cluded 35 from Figure 3 (those without backup filters were excluded), plus 6 additional distributions reported too recently for inclusion in Figure 3.

The three categories of the lead distributions all show similar shapes, with a peak between 0.5 and 1 μm aerodynamic diameter. The similarity in the distributions reflects the fact that anthropogenic combustion processes are the primary sources of airborne lead at virtually all sites sampled, including those far from emissions. In contrast, average spectra for sodium and aluminum, also shown in Figure 4, show generally larger particles and greater variability. Sodium is derived from crustal weathering and sea spray, while aluminum is derived mostly from crustal weathering.

It is worthwhile to consider uncertainties in these size distribution data. Table 3 shows that nearly all of the data were obtained with cascade impactors. These devices fractionate airborne particles according to their aerodynamic diameters, operating by the mechanism of inertial impaction. An impactor system may be composed of several cascaded stages, each stage collecting smaller particles than the one above, with a final backup filter to collect very small particles. While providing a convenient method of fractionating aerosols for subsequent elemental analysis, impactors are highly imperfect.

One difficulty with impactor sampling concerns the upper end of the size spectrum. Obtaining a representative sample of large airborne particles requires careful measuring techniques. The air velocity at the impactor inlet must be approximately the same as the ambient wind speed (isokinetic sampling), and the inlet must be directionally aligned with the wind (Liu and Pui, 1981). Even with these precautions, particle loss within the inlets may occur

(Felix and McCain, 1981). Additional losses of large particles on the inner walls of impactors have been reported by McFarland et al. (1977), Cushing et al. (1979) and Chan and Lawson (1981).

Another problem with impactors is that particle bounceoff inside the units may occur. Large particles may make their way down to the lower impactor stages or onto the backup filter, biasing the distribution toward small particle sizes. Bounceoff may be especially severe in high-volume impactors. The problem can be minimized by use of adhesive-coated collection substrates on each impactor stage (Wesolowski, 1973; Dzubay et al., 1976; Lawson, 1980). Because of the potential contamination and handling problems associated with adhesives, such precautions are not always implemented.

There is also evidence that glass fibre filters may decrease bounceoff relative to smoother surfaces such as cellulose (Sievering et al., 1978). However, Rao (1975) and Dzubay et al. (1976) showed that glass fibre substrates may collect particles smaller than the rated cutoff diameters, due to filtration as the airstream penetrates the fibrous material. Additional studies have suggested that impactor sampling of marine aerosol with cellulose filter substrates may not be appreciably influenced by bounceoff; high humidities which moisten the cellulose filters, as well as the hygroscopic nature of marine aerosol, are believed responsible (Walsh et al., 1978).

Collection efficiency curves for typical impactors show that with proper operation, the devices generally fractionate aerosols into the approximate desired size ranges. But even with careful sampling and proper choice of substrate material, the fractionation is highly imperfect. Small particles may be collected to a certain extent on the upper impactor stages, while some of the large particles may not be impacted until reaching the lower stages. Such problems are the result of non-ideal airflow through the impactor, particularly variations in the air velocity across each jet (Marple and Liu, 1974; Marple et al., 1974). Collection efficiency curves for typical impactors, generated with monodisperse particles in the laboratory, have been presented by May (1964), Flesch et al. (1967), Swartz et al. (1973) and Knuth (1979), and in many of the studies referenced above.

Most of the size distribution data in Figures 3 and 4 have been obtained using techniques that are far from ideal. Very few of the studies attempted to sample large particles accurately; most incorporated vertically oriented inlets. Some of the samplers used rainshields above the inlets, further reducing the collection efficiency of large particles. Impactor substrates included metal plates, Teflon film, polyethylene film, cellulose filters and glass fibre filters which in general were not coated with adhesive material. Several of the investigators made no attempt to calibrate their impactors, relying instead upon manufacturers' suggested cutoff diameters. Possible errors in airflow rates may have resulted in additional uncertainty in the cutoff diameters. Because of these problems, the data in Figures 3 and 4 must be regarded as rough approximations to the true distributions.

Use of Airborne Size Data to Predict Deposition

The size distributions in Figures 3 and 4 have been used to perform two types of calculations. Firstly, the fractional deposition in each compartment of the human lung has been estimated, allowing assessment of the amount of lead inhaled. Secondly, dry deposition velocities for transport from the atmosphere onto various surfaces have been calculated.

Deposition in the Lung

Trace metal deposition in the human respiratory tract has been studied previously by Natusch and Wallace (1974). These investigators used the model of the International Commission on Radiological Protection (ICRP) with size distribution estimates for lead, iron and other species to predict deposition in the nasopharyngeal, tracheobronchial and pulmonary compartments of the lung. Their results suggest that lead, predominantly on submicrometre particles, is deposited to an appreciable extent in the pulmonary compartment. The ICRP model indicates a fractional mass deposition (mass deposited/mass inhaled) in the range 0.25-0.65 for submicrometre particles in this region, with much smaller fractions depositing in the other compartments (Task Group on Lung Dynamics, 1966). The deposition of iron, on the other hand, is more pronounced in the nasopharyngeal region due to greater airborne mass in large particles.

Akselsson et al. (1976), Desaedeleer and Winchester (1975) and Desaedeleer et al. (1977) compared the concentrations of several trace metals as a function of particle size in inhaled and exhaled air. Their results suggest that deposition in the total respiratory tract is minimal for particles with $d_p \sim 0.5$ µm. The fractional mass deposition is less than 0.5 for this particle diameter. Slightly greater values are observed for smaller particles, while values as large as 0.96 are associated with particles of aerodynamic diameter greater than 4 µm.

New data for particle deposition in the lung have become available since these studies were published. Of particular importance is the work of Lippmann (1977), Chan and Lippmann (1980) and Stahlhofen et al. (1980). These investigators reported experimental data for monodisperse particle deposition in each compartment of the human lung, which can be used with published size distribution data to calculate respiratory tract deposition.

The results of these lung deposition studies, summarized EPA (1982), have been used with the distributions in Figures 3 and 4 to estimate the fractional mass deposition for lead. In performing these calculations, the geometric mean particle diameter for each size interval has been used as the basis for estimating the mass deposition fraction f_i for that interval. Only lung deposition data for mouth breathing have been used to estimate the various f_i values. The final deposition fraction F for each compartment of the lung, for each distribution, has been computed from the relation:

$$F = \sum_{i=1}^{n} f_i \; C_i \Big/ \sum_{i=1}^{n} C_i \qquad (2)$$

where C_i is the airborne mass concentration of lead in size range i. The values of F thus refer to the total mass of lead deposited in a specific compartment of the lung divided by the total mass of the metal inhaled. The applicable respiration rates range from 7.5 to 30 L min^{-1}, with tidal volumes generally in the range 1.0-1.5 L.

Results of this calculation are shown in Figure 5. Besides lead, the computations have been performed for cadmium, copper, iron, manganese, and zinc using size distributions taken from the literature for each of these elements (Davidson and Osborn, 1986). Minimum and maximum pulmonary deposition fractions are based on the two pulmonary deposition curves which envelop the data, as reported by the US Environmental Protection Agency (EPA, 1982). Values for each of the three compartments have been summed to obtain the total deposition fractions.

Of primary interest is the surprisingly uniform average deposition fraction in the pulmonary compartment for all six metals. The minimum fraction is

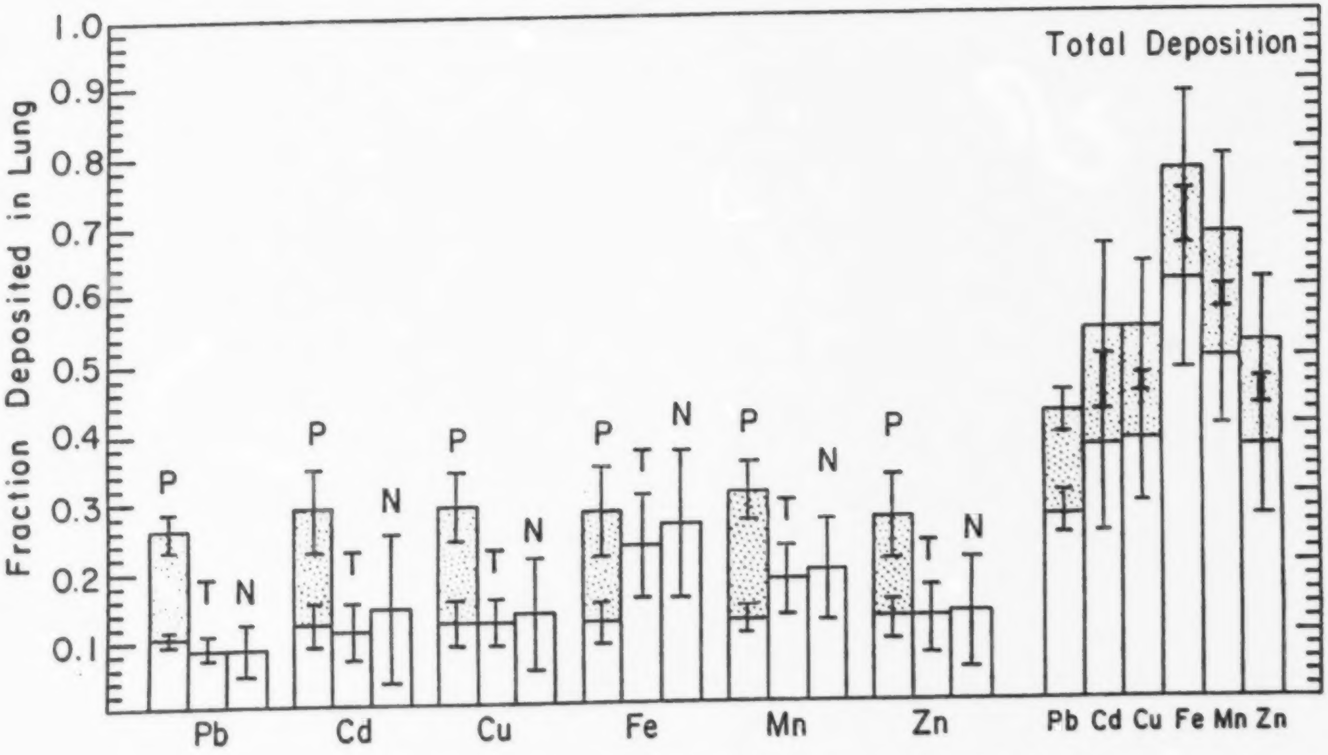

Figure 5. Deposition in Pulmonary, Tracheobronchial, and Nasopharyngeal Compartments.

in the range 0.10-0.12, whereas the maximum is in the range 0.26-0.30. This uniformity is in contrast to the calculations of Natusch and Wallace (1974), who report a pulmonary deposition fraction of 0.32 for lead but only 0.22 for iron. The differences between the Figure 5 results and the earlier calculations reflect the relatively small deposition fractions for submicrometre particles reported in the recent lung deposition studies: the new pulmonary compartment data show deposition fractions below 0.2 for particles smaller than 0.5 μm, with a peak in the range 0.3-0.6 at approximately 3 μm. The ICRP model, in contrast, predicts a steadily increasing pulmonary deposition fraction as particle size decreases, reaching 0.4 at 0.1 μm. Chan and Lippmann (1980) stated that the ICRP model overestimates pulmonary deposition by at least a factor of two for particles smaller than 0.5 μm. Such differences are likely to have a marked effect on the calculated pulmonary deposition of lead, a predominantly submicrometre species.

The tracheobronchial deposition fractions in Figure 5 are in the range 0.081-0.12 for lead, cadmium, copper, and zinc, with somewhat larger fractions for manganese and iron. These values reflect the increasing tracheobronchial deposition with increasing particle size up to approximately 8 μm. Similar trends are observed for deposition in the nasopharyngeal compartment, and for total deposition in all compartments of the respiratory tract. Note that deposition in the nasopharyngeal compartment is only slightly greater than that in the tracheobronchial compartment for each metal.

It is worthwhile to consider the limitations of the lung deposition calculations discussed above. Of primary importance are the inaccuracies associated with the size distribution data. For example, the lack of detailed information on the distribution of particles within each size interval has necessitated the use of the geometric mean particle diameter when estimating lung deposition. It is fortunate that the interval corresponding to the backup filter, which generally encompasses the widest size range, may not be as significant as the supermicrometre size ranges for the calculations of Figure 5; the lung deposition data for submicrometre particles show relatively small fractions depositing, and show roughly constant deposition across a wide range of particle sizes. The error introduced by using aerodynamic as opposed to geometric diameters for these submicrometre particles is also likely to be small. However, the uncertainty caused by using the geometric mean particle diameter for the uppermost impactor stage may have been significant for the calculated tracheobronchial and nasopharyngeal deposition rates. Related to this problem is the poor sampling efficiency for the largest airborne particles in the distributions, which may have resulted in calculated deposition fractions which are smaller than the true values.

Another problem concerns the enrichment of volatile species such as lead on the surfaces of particles, resulting from condensation of gases containing these species. Such surface coatings may be more readily available for absorption than material composing the bulk of each particle (Natusch and Wallace, 1974; Linton et al., 1976; Van Craen et al., 1983), complicating the interpretation of Figure 5.

A third problem concerns uncertainties in the lung deposition data. Especially important is the difficulty in generalizing the data, derived from a limited number of subjects, to a larger population. Because of these problems, the results of Figure 5 must be viewed cautiously.

Deposition from the Atmosphere onto Surfaces

The distributions in Figures 3 and 4, and similar distributions for cadmium, copper, iron, manganese, and zinc, have also been used with dry deposition models to estimate the deposition of each trace metal onto several types of surfaces. These calculations have been performed in a manner similar to the lung deposition estimates, using the geometric mean diameter for each size interval as the basis for estimating the dry deposition velocity v_{di} for that interval. The overall dry deposition velocity V_d for each distribution has been calculated from the relation:

$$V_d = \sum_{i=1}^{n} v_{di} \Delta C_i \Big/ \sum_{i=1}^{n} \Delta C_i \qquad (3)$$

Five different sets of v_{di} have been used for these calculations. The first two sets involve the model of Davidson et al. (1982) for *Agrostis hyemalis* (hair grass) and *Andropogon virginicus* (broom sedge), species of wild grass. This model incorporates equations of particle transport by diffusion, interception, impaction and sedimentation to predict dry deposition; data for the geometry of the vegetation and for windfield characteristics above and within the canopies have been applied. The third set of v_{di} values is derived from the model of Sehmel and Hodgson (1978). These investigators developed empirical equations applicable to a wide variety of conditions, based on their wind tunnel data for monodisperse particle deposition onto several types of surfaces. The fourth set is based on the model of Slinn (1982) for a *Eucalyptus* forest. This investigator used detailed equations of particle transport with measured wind speed profiles and assumed geometrical characteristics of the forest to estimate dry deposition. The final set of v_{di} values is based on sedimentation, providing an estimate of the minimum dry deposition expected.

Results of these calculations are shown in Table 4. The values of V_d for the individual distributions have been averaged for each metal and for each surface type to yield these results. Values of the relevant parameters for each set of atmospheric and surface conditions are given in the table: h is the average height of the vegetation, d is the zero plane displacement of the canopy, z_0 is the roughness height (i.e. momentum sink) and u_* is the friction velocity. All of the models are based on an adiabatic atmosphere. For each of the five surfaces, the total deposition velocities increase in the order $Pb \sim Cd \sim Cu \sim Zn < Mn < Fe$, a pattern consistent with the differences in particle size for each element. These calculations further show that the largest particles in each distribution are responsible for most of the dry deposition mass.

For lead, the large particles influencing deposition constitute only a small fraction of the total airborne lead mass. This suggests that the denominator of Eq. (3) should be reduced to include only the uppermost size ranges if a meaningful deposition velocity is to be calculated: the small V_d values for lead in Table 4 do not reflect predominant deposition of small particles, but rather deposition of fewer large particles.

Table 4 shows much smaller deposition velocities for Andropogon virginicus than for Agrostis hyemalis. The difference is due to the greater leaf area index of Agrostis, as well as the presence of fine hairs which assist particle capture. The model of Sehmel and Hodgson (1978) provides results which are comparable with those of Andropogon, while sedimentation yields values approximately one-third as large. It is interesting and somewhat surprising that deposition velocities for Agrostis are actually slightly greater than those of the Eucalyptus forest. Although this comparison is tenuous because of different assumptions in the two models, Slinn (1982) calculated deposition velocities for grass and wheat as well as for Eucalyptus, and the results show values for the shorter canopies which are comparable with those of the forest. Relatively small wind speeds within the Eucalyptus canopy, as well as assumed characteristics of the vegetation geometry, are apparently responsible for keeping the deposition velocities small.

Several difficulties with these dry deposition estimates, similar to problems encountered with the lung deposition calculations, must be considered. A major problem concerns inaccuracies in the measured size distribution data for lead and the other metals. Difficulties in sampling the largest airborne particles, which greatly influence deposition, may have compromised the calculations. The deposition models must also be acknowledged as major sources of uncertainty. The models of Davidson et al. (1982) and Slinn (1982) involve numerous assumptions, and have never been tested experimentally. The model of Sehmel and Hodgson (1978) involves the tenuous extrapolation of experimental data for slightly rough artificial surfaces in a wind tunnel to much rougher natural vegetation exposed to the ambient atmosphere. As such, the results presented in Table 4 must be viewed with caution.

Summary

This report has reviewed data for atmospheric lead in several sections. First, airborne concentrations in urban, rural and remote areas have been summarized. Urban area lead concentrations are generally in the range 1-10 μg m^{-3}, with rural concentrations in the range 0.1-1 μg m^{-3}. Remote area levels range from 0.001 to 0.1 μg m^{-3}. Airborne lead data prior to the 1970s are probably less reliable than more recent data, due to improvements in sampling, sample handling and analytical techniques.

In the second section, airborne size distributions of lead have been summarized. The distributions show that lead is primarily submicrometre, with the shape of the spectra nearly identical in urban, marine and non-urban continental locations. lead is generally associated with smaller particles than soil-derived or sea-spray-derived elements. For example, lead has an overall mass median aerodynamic diameter of 0.55 μm (average for 41 distributions), while sodium and aluminum have mass median aerodynamic diameters averaging 3.8 and 4.5 μm, respectively.

In the final section, the size distributions have been used to calculate deposition in the human lung and dry deposition onto natural surfaces. Results of these calculations show that lead is deposited with efficiencies as great as 26% in the pulmonary region, but with less than 10% efficiency in the tracheobronchial or nasopharyngeal regions of the human respiratory system. The total deposition efficiency in all three regions is about 40%. For comparison, the metals cadmium, copper, iron, manganese and zinc are deposited with similar efficiencies in the pulmonary compartment, although iron and manganese have significantly greater deposition efficiencies than lead in the tracheobronchial and nasopharyngeal regions due to their larger particle sizes. The small particle size of lead also influences dry deposition onto natural surfaces. Deposition velocities for natural grass canopies are less than 1 cm s^{-1} for lead, but may be as great as several centimetres per second for iron, manganese, and other crustally derived elements. Dry deposition of lead onto other natural surfaces is also likely to be much smaller than that of elements associated with larger particles.

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Table 1.

Atmospheric lead in urban and rural areas (after Nriagu, 1978).

Location	Sampling Period	Lead Conc. ($\mu g\ m^{-3}$)	Reference
Berlin (busy streets)	1966-67	3.8	From Blokker, 1972
(quiet streets)	"	0.4-0.5	"
Frankfurt (residential area)	1969-70	0.8	Georgii and Jost, 1971
(heavy traffic)	1979-72	2.7	Jost et al., 1973
Hamburg (quiet streets)	1961-62	2.0	From Blokker, 1972
Vienna	1969-70 (winter)	2.6 (0.2-14.0)	Hartl and Resch, 1973
	1970 (summer)	2.9 (0.8-6.6)	"
Zurich (urban areas)	1950	1.5	Hogger, 1973
	1963	2.7	"
	1970	3.8	"
Rotterdam (10-15 m above street)	1968	0.4	From Blokker, 1972
Brussels (residential)	1972	1.9	Janssens and Dams, 1975
Ghent (residential)	"	1.2	"
(industrial)	"	0.9	"
Antwerp (residential)	"	2.7	"
(industrial)	"	1.2	"
Liege (residential)	"	2.0	"
(residential)	1968-69	0.8	Rondia and de Graeve, 1973
(industrial)	"	1.8	"
	1972	2.7	"
Charleroi (residential)	"	1.7	"
Belgium (background level)	"	0.23	"
The Hague (downtown)	1970-71	1.2	Guicherit, 1973
(residential)	"	0.4	"
Amsterdam (Christiaan Huygensstr.)	1971	0.9	"
Zagreb (urban)	1970-71 (winter)	1.5	Fugas et al., 1973
	1970-71 (summer)	0.6	"
Tula (before ban-leaded gasoline)	-	1.4	From Waldron and Stofen, 1974
(after ban-leaded gasoline)	-	0.24	"
Chelyabinsk	-	3.9	"
Turin (urban)	1974	5.0 (1.5-8.1)	Magi et al., 1975
Rome (downtown sites)	1972-73	4.5 (0.1-28)	Colacino and Lavagnini, 1974
Milan (urban)	1956	2.4-7.4	Giubileo, 1957

Table 1. (Cont'd)

Genoa (urban)	1965	7.4-14.2	Petrilli et al., 1966
Paris (central streets)	1964	4.6	From Blokker, 1972
(Gif-sur-Yvette)	1968	1.4	Servant, 1973
Tulane	"	0.01-1.0	"
London (Fleet Street)	1964	3.2	From Blokker, 1972
(Fleet Street)	1971-72	3.7	Lawther et al., 1973
(Medical College)	"	0.8	"
(downtown)	1972	5.1	Harrison et al., 1974
(Heathrow airport)	"	1.7	"
(tunnel, Heathrow airport)	"	32.2	"
UK (rural locations)	1956-58	0.29	Stocks et al., 1961
	1972	0.13	Cawse, 1974
	1973	0.13	"
Central Swansea	1972-73	0.61	Pattenden, 1974
Miami	1974	1.3 (0.8-1.8)	HASL, 1975
New York	"	1.08 (0.9-1.4)	"
New York (central city)	1954; 1956	2.1 (0.2-8.9)	DHEW, 1958
(city-wide average)	1960-65	4.1 (1.0-13.2)	Colucci et al., 1969
(3 metro sites)	1968	3.1 (0.11-5.03)	Kneip et al., 1970
(5 metro sites)	1969-70	1.3 (0.6-2.5)	Morrow and Brief, 1971
(metro sites)	1972-73	1.7 (0.3-2.1)	Kneip and Eisenbud, 1974
New York Bight	1974	0.13 (0.02-0.3)	Duce et al., 1975
Washington, D.C. (NASN Stations)	1970	0.6	Lee et al., 1972
Boston (downtown)	1972	4.5 (2.3-18.9)	O'Brien et al., 1975
Framingham, Mass. (rural)	"	0.9 (0.3-5.0)	"
Lawrence, Mass. (semi-urban)	"	1.1 (0.4-9.9)	"
Cambridge, Mass. (industrial)	1969	1.91 (0.39-3.7)	Moyers et al., 1972
(residential)	1965	0.8 (0.08-2.3)	Lininger et al., 1966
St. Louis (downtown)	1973	1.07	Tanner et al., 1974
(32 km downwind)	"	0.17	"
(64 km downwind)	"	0.20	"
(97 km downwind)	"	0.16	"
(NASN Stations)	1970	1.1	Lee et al., 1972
Columbia, S. Carolina (downtown)	1974-75	1.4 (0.6-2.6)	Kinard et al., 1976
Cincinnati (residential)	1946-51	1.9 (1.6-2.5)	Cholak, 1964
(industrial)	"	3.5 (3.0-4.1)	"
(rural)	"	1.1 (0.8-1.3)	"
(city-wide average)	"	2.7 (0.8-4.1)	"
(NASN Stations)	1970	1.8	Lee et al., 1972
(4 metro sites)	1961-62	1.4 (0.3-6.4)	From Colucci et al., 1969

Table 1. (Cont'd)

Philadelphia (7 metro sites)	1960-65	1.6 (0.1-7.6)	From Colucci et al., 1969
Detroit (central city)	1953-54	2.4 (0.2-5.8)	DHEW, 1958
(3 metro sites)	1960-65	4.8 (1.0-11.8)	Colucci et al., 1969
Chicago (city-wide average)	1964	0.9	Winchester and Nifong, 1971
	1968	3.7 (0.3-7.0)	Harrison and Winchester, 1971
(NASN Stations)	1970	1.1	Lee et al., 1972
Urbana-Champaign (residential)	1973-74	0.23 (0.06-0.5)	Hudson et al., 1975
Ann Arbor (residential)	1968	0.6-6.0	Harrison et al., 1971
Helena, Montana	1974	0.35 (0.2-0.6)	HASL, 1975
Chadron, Nebraska (rural)	1973-74	0.045 (0.009-0.09)	Struempler, 1975
Salt Lake City	1974	0.89 (0.6-1.2)	HASL, 1975
Denver (urban sites)	1969	0.2-8.0	Parungo and Rhea, 1970
(NASN Stations)	1970	0.8	Lee et al., 1972
San Francisco Bay area	1971	0.84 (0.3-1.6)	Martens et al., 1973
Los Angeles (downtown)	1954	3.6 (0-14.1)	DHEW, 1958
	1954-55	6.6 (1.0-13)	Cholak, 1964
	1961-62	4.3 (1.0-13)	"
	1960-65	7.6 (0.4-18.4)	Colucci et al., 1969
	1963 (daytime)	5.6	Robinson et al., 1963
	1968-69	3.6	From Chow, 1973
San Diego (downtown)	1971	2.1	"
La Jolla (Scripps Pier)	"	0.42	"
Pasadena (Caltech campus)	1972	2.14 (0.2-8)	Hammerle and Pierson, 1975
Fairbanks, Alaska (downtown)	1965	3.7 (1.3-6.0)	Winchester et al., 1967
(Univ. campus)	"	0.3 (0.2-0.43)	"
Honolulu (urban sites)	1970	1.64 (0.08-6.1)	Jernigan et al., 1971
(curb-sides)	"	7.73 (2.0-13.8)	"
Rio de Janeiro (city centre)	1972-73	0.8	Branquinho and Robinson, 1976
(industrial)	"	1.5	"
(suburban)	"	0.3	"
Ottawa (downtown)	1975 (Jan-Dec)	1.3	From Environment Canada, 1975
Windsor (3 sites)	"	0.54	"
Kingston (Queen's Univ.)	"	0.28	"
Toronto (3 sites)	"	1.3	"
Hamilton (residential)	"	1.0	"
Sudbury (2 sites)	"	0.57	"
Thunder Bay (Algoma St.)	"	0.53	"
Winnipeg (4 sites)	"	0.78	"
Saskatoon (residential)	"	0.32	"
Edmonton (5 sites)	"	0.26	"

Table 1. (Cont'd)

Vancouver (several sites)	1975 (Jan-Dec)	1.0	From Environment Canada, 1975
Halifax (residential)	"	0.28	"
Montreal	"	2.0	"
Quebec City (downtown)	"	1.4	"
Saint John's (downtown)	"	0.67	"
Yellowknife (residential)	"	0.33	"
Moose Jaw (Telephone bldg.)	"	0.32	"
Lethbridge (residential)	"	0.22	"
Toronto (downtown commercial)	1973	1.6	Ogner et al., 1975
(residential)	"	1.0	"
(suburban)	"	0.6	"
(expressway)	"	2.1	"
(near lead smelter)	"	12.4	"
Balboa, Panama	1974	0.24 (0.18-0.30)	HASL, 1975
	1967	0.23	Harley, 1970
Guayaquil, Ecuador	1974	0.29 (0.15-0.35)	HASL, 1975
	1967	0.35	Harley, 1970
Lima, Peru	1974	0.43 (0.31-0.51)	HASL, 1975
	1967	0.50	Harley, 1970
Chacaltaya, Bolivia	1974	0.037 (0.018-0.076)	HASL, 1975
	1967	0.09	Harley, 1970
Antofagasta, Chile	1974	0.034 (0.022-0.047)	HASL, 1975
	1967	0.06	Harley, 1970
Santiago, Chile	1975	0.75 (0.45-1.01)	HASL, 1975
	1967	0.87	Harley, 1970
Puerto Montt, Chile	1975	0.012 (0.009-0.015)	HASL, 1975
Punta Arenas, Chile	"	0.068 (0.051-0.087)	"
	1967	0.06	Harley, 1970
Bimini, The Bahamas	"	0.10	"
San Juan, Puerto Rico	"	0.80	"
Rio de Janeiro (industrial)	1972-73	1.5	Branquinho and Robinson, 1976
(city centre)	"	0.48	"
(residential)	"	0.70	"
(road tunnels)	"	64-99	"

Table 2.

Atmospheric lead in remote areas (after Wiersma and Davidson, 1985).

Location	Sampling Period	Lead Conc. ($ng\ m^{-3}$)	Reference
Arizona, rural area	Jan-Dec 1974	67	Moyers et al., 1977
California, High Sierra	Jun & Aug 1976, Aug 1977	21	Elias and Davidson, 1980
Florida, Apalachicola Natl. Forest	May-Jul 1973	26	Johansson et al., 1976
Hawaii, coast	-	1.2	Gordon et al., 1978
Michigan, Seney Natl. Wildlife Refuge	Jun 1979	10	Alkezweeny et al., 1982
Montana, Colstrip	May-Sep 1975	14	Crecelius et al., 1980
Montana, Glacier Natl. Park	Aug 1981	4.6	Davidson et al., 1985
Tennessee, Smoky Mts. Natl. Park	Oct 1979	19	"
Tennessee, Smoky Mts. Natl. Park	Sep 1978	111	Stevens et al., 1984
Utah, Canyonlands	Jul 1977-Dec 1978	30	Flocchini et al., 1981
Utah, Henrieville	Jul 1977-Sep 1978	72	"
Utah, Zion Natl. Park	Oct 1977-Dec 1978	48	"
Virginia, Shenandoah Valley	Jul-Aug 1980	61	Stevens et al., 1984
Washington, Olympic Natl. Park	Jul-Aug 1980	2.2	Davidson et al., 1985
Washington, Quillayute, onshore wind	Apr 1974-Jun 1975	1.8	Ludwick et al., 1977
Antarctica	Dec 1974-Feb 1975	0.027	Maenhaut et al., 1979
Arctic (Canadian)	Late winter 1980	1.0	Barrie et al., 1981
Atlantic Ocean, East	-	7	Duce et al., 1976
Bermuda	Summer 1975	7	"
Bolivia, Chacaltaya Mt.	Feb-May 1976	3.7	Adams et al., 1977
China, Great Wall	Apr 1980	5.6	Winchester et al., 1981
Enewetak	Apr-May 1979	0.13	Duce et al., 1983
Enewetak	Jun-Aug 1979	0.096	"
Enewetak	Apr-May 1979	0.23	Settle and Patterson, 1982
Enewetak	Jul-Aug 1979	0.12	"
Greenland, Dye 3	Jun-Aug 1979	0.15	Davidson et al., 1981b
Greenland, Kap Harald Moltke	Jun-Aug 1974	0.20	Flyger and Heidam, 1978
Greenland, Thule	Feb-Apr 1978	8.0	Heidam, 1981
Greenland, Prins Christianssund	Jan-Feb 1978	1.8	"
Nepal, Himalayas	Dec 1979	0.86	Davidson et al., 1981a
Norway, Birkenes	Sep-Dec 1974, Apr-May 1975	17	Thrane, 1978
Norway, Birkenes	Autumn 1973	24	Semb, 1978
Spitzbergen	Dec 1973-Mar 1974	5.8	Larssen, 1977
Spitsbergen	Apr-May 1979	< 4.9	Heintzenberg et al., 1981
Sweden, Sjoangen	Annual avg.	21	Lannefors et al., 1983
USSR, Abastumani Mts.	Jul 1979	19	Stevens et al., 1984

Table 3.

Information associated with the airborne mass distributions in Figure 3. All impactors and cyclones were operated with backup filters, unless otherwise indicated. The Andersen impactors refer to the standard 1 CFM samplers (28 L min^{-1}), while the Sierra high-volume impactors are the slotted 40 CFM devices (1100 L min^{-1}). Other samplers listed in this table include the cyclone system of Bernstein and Rahn (15-210, L min^{-1}), the Lundgren impactor (82 L min^{-1}), the Casella impactor (17 L min^{-1}), the Scientific Advances impactor (12 L min^{-1}), and the Delron Battelle-type impactor (1 L min^{-1}). These airflows represent the manufacturers' rated values; actual flow rates were often different from these ratings (Davidson and Osborn, 1985).

Graph No.	Reference	Dates of Sampling	Location of Sampling	Type of Sampler
1	Lee et al., 1972	Jan.-Dec. 1970 Average of 4 quarterly composited samples, representing a total of 21 sampling periods of 24 h each	Chicago, Illinois	Andersen impactor operated at 5-6 CFM
2	Lee et al., 1972	Mar.-Dec. 1970 Same averaging as Graph 1, total of 18 sampling periods	Cincinnati, Ohio	Same as Graph 1
3	Lee et al., 1972	Jan.-Dec. 1970 Same averaging as Graph 1, total of 21 sampling periods	Denver, Colorado	Same as Graph 1
4	Lee et al., 1972	Mar.-Dec. 1970 Same averaging as Graph 1, total of 20 sampling periods	Philadelphia, Pennsylvania	Same as Graph 1
5	Lee et al., 1972	Jan.-Dec. 1970 Same averaging as Graph 1, total of 22 sampling periods	St. Louis, Missouri	Same as Graph 1

6	Lee et al., 1972	Jan.-Dec. 1970 Same averaging as Graph 1, total of 23 sampling periods	Washington, D.C.	Same as Graph 1
7	Lee et al., 1972	September 1966 Average of 14 runs, 24 h each	Cincinnati, Ohio	Andersen impactor 1.2 m above the ground
8	Lee et al., 1972	February 1967 Average of 3 runs, 4 d each	Fairfax, Ohio, suburb of Cincinnati	Same as Graph 7
9	Peden, 1977	Summer 1975 Average of 4 runs, average 8 d each	Alton, Illinois, industrial area near St. Louis	Andersen impactor, no backup filter
10	Peden, 1977	Summer 1972 Average of 3 runs, average 10 d each	Centreville, Illinois downwind of a zinc smelter	Andersen impactor, with backup filter
11	Peden, 1977	Summer 1973 Average of 2 runs, average 5 d each	Collinsville, Illinois, industrial area near St. Louis	Same as Graph 10
12	Peden, 1977	Summer 1973 Average of 2 runs, average 6 d each	KMOX radio transmitter, Illinois, industrial area near St. Louis	Same as Graph 10
13	Peden, 1977	Summer 1972 Average of 9 runs, average 9 d each	Pere Marquette State Park, Illinois, upwind of St. Louis	Same as Graph 10
14	Peden, 1977	Summer 1975 Average of 4 runs, average 8 d each	Wood River, Illinois, industrial area near St. Louis	Same as Graph 9

15	Cholak et al., 1968	April 1968 Average of several runs, 3 d each	3 sites: 10,400 and 3300 m from Interstate 75, Cincinnati, Ohio	Andersen impactor
16	McDonald and Duncan, 1979	June 1975 One run of 15 d	Glasgow, Scotland	Casella impactor 30 m above the ground
17	Dorn et al., 1976	Winter, spring, summer 1972 Average of 3 runs, 27 d each	Southeast Missouri, 800 m from a lead smelter	Andersen impactor 1.7 m above the ground, no backup filter
18	Dorn et al., 1976	Winter, spring, summer 1972 Average of 3 runs, 14 d each	Southeast Missouri, 75 km from the lead smelter of Graph 17	Same as Graph 17
19	Daines et al., 1970	1968 Average of continuous 1-week runs over an 8-month period	3 sites: 9, 76 and 530 m from US Route 1, New Brunswick, New Jersey	Cascade impactor 1.2 m above the ground
20	Martens et al., 1973	July 1971 One run of 4 d	9 sites throughout San Francisco area	Andersen impactor
21	Lundgren, 1970	November 1968 Average of 10 runs, 16 h each	Los Angeles, California	Lundgren impactor
22	Huntzicker et al., 1975	May 1973 One run of 8 h	Shoulder of freeway near downtown Los Angeles, California	Andersen impactor 2 m above the ground
23	Huntzicker et al., 1975	February 1974 One run of 6 d	Pasadena, California	Andersen impactor on roof of 4-storey building
24	Davidson, 1977	May and July 1975 Average of 2 runs, 61 h each	Pasadena, California	Modified Andersen impactor on roof of 4-storey building

25	Davidson et al., 1980	October 1979 One run of 120 hours	Clingman's Dome, Great Smokies National Park, elev. 2024 m	2 modified Andersen impactors 1.2 m above the ground
26	Davidson et al., 1981c	July-Sep. 1979 Average of 2 runs, 90 h each	Pittsburgh, Pennsylvania	Modified Andersen impactor 4 m above the ground
27	Davidson et al., 1981a	December 1979 One run of 52 h	Nepal Himalayas, elev. 3962 m	Modified Andersen impactor 1.2 m above the ground
28	Davidson et al., 1983	June 1980 One run of 72 h	Export, Pennsylvania, 40 km east of downtown Pittsburgh	2 modified Andersen impactors 1.2 m above the ground
29	Davidson et al., 1985	July 1980 One run of 34 h	Packwood, Washington, rural site in Gifford Pinchot National Forest	Modified Andersen impactor 1.5 m above the ground
30	Davidson et al., 1985	July-Aug. 1980 One run of 92 h	Hurricane Ridge, Olympic National Park, elev. 1600 m	Modified Andersen impactor 1.5 m above the ground
31	Duce et al., 1976	May-June 1975 One run of 112 h	Southeast coast of Bermuda	Sierra high-volume impactor 20 m above the ground
32	Duce et al., 1976	July 1975 One run of 79 h	Same as Graph 31	Same as Graph 31
33	Harrison et al., 1971	April 1968 Average of 21 runs, 2 h each	Ann Arbor, Michigan	Modified Andersen impactor 20 m above the ground
34	Gillette and Winchester, 1972	October 1968 Average of 15 runs, 24 h each	Ann Arbor, Michigan	Andersen impactor near ground level
35	Gillette and Winchester, 1972	- -	Chicago, Illinois	Same as Graph 34

36	Gillette and Winchester, 1972	- -	Lincoln, Nebraska	Same as Graph 34
37	Johansson et al., 1976	June-July 1973 Average of 15 runs, average 50 h each	2 sites in Tallahassee, Florida	Delron Battelle-type impactor on building roofs, no backup filter
38	Cawse, 1974	July-Dec. 1973	Chilton, England	Andersen impactor 1.5 m above the ground
39	Pattenden, 1974	May-Aug. 1973 Average of 4 runs, 1 month each	Trebanos, England	Same as Graph 38
40	Bernstein and Rahn, 1979	August 1976 Average of 4 runs, 1 week each	New York City, New York	Cyclone system on roof of 15-storey building

Table 4.

Average and standard deviation of the dry deposition velocity (cm s^{-1}) calculated using deposition models for several types of surfaces (after Davidson and Osborn, 1985).

Metal	n	*Agrostis hyemalis* h=33 cm, d=13 cm z_o=14 cm u_*=40 cm s^{-1} (Davidson et al., 1982)	*Andropogen virginicus* h=57 cm, d=14 cm z_o=9 cm u_*=32 cm s^{-1} (Davidson et al., 1982)	Extrapolation from wind tunnel data for various surfaces z_o=3 cm u_*=30 cm s^{-1} (Sehmel and Hodgson, 1978)	*Eucalyptus* forest h=27.4 m, d=21.6 m z_o=1.86 m u_*=75 cm s^{-1} (Slinn, 1982)	Sedimentation (Friedlander, 1977)
Pb	35	0.96 ± 0.40	0.20 ± 0.15	0.20 ± 0.092	0.28 ± 0.20	0.060 ± 0.063
Cd	17	1.5 ± 0.83	0.32 ± 0.30	0.30 ± 0.18	0.45 ± 0.40	0.10 ± 0.12
Cu	19	1.5 ± 0.65	0.29 ± 0.23	0.29 ± 0.14	0.43 ± 0.33	0.087 ± 0.085
Fe	29	2.7 ± 0.87	0.59 ± 0.30	0.54 ± 0.18	0.85 ± 0.47	0.17 ± 0.11
Mn	18	2.1 ± 0.63	0.41 ± 0.18	0.43 ± 0.14	0.62 ± 0.30	0.12 ± 0.066
Zn	26	1.5 ± 0.73	0.32 ± 0.31	0.29 ± 0.17	0.44 ± 0.40	0.10 ± 0.13

5. ATMOSPHERIC DEPOSITION OF LEAD IN LAKE SEDIMENTS AND PEAT

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Introduction

Although local lead pollution of aquatic systems from stationary point sources has been well known for the last 30-40 years, and has been documented by studies of stream and lake sediments, only in the last 15 years has the regional nature of the pollution been documented. In addition to studies of forest soils (Siccama et al., 1980), lichens and mosses (Lawrey and Hale, 1981; Groet, 1976), it has been documented by the study of cores of lake sediments and ombrotrophic peat. Both types of study enable the development of a historical perspective for atmospheric loading of lead because of the continued accumulation of sediment or peat. Studies of the 'instantaneous' spatial distribution pattern of atmospherically derived lead can also be obtained from analyses of the lead content of mosses (Groet, 1976) and forest floor (Johnson et al., 1982; Hanson et al., 1982). These studies showed deposition rates of 1-7 $\mu g\ cm^{-2}\ a^{-1}$ for the spruce-fir forests of Vermont. Repetition of soil surveys has enabled some estimate of the atmospheric loading rates to those types of surfaces, averaged over 10-15 years (Siccama et al., 1980; Friedland et al., 1984). Lawrey and Hale (1981) and others have attempted to determine atmospheric deposition rates for lead utilizing slowly growing lichens as collectors of pollutants.

In the absence of systematic, geographically widespread and continuous monitoring of the atmospheric deposition of lead (e.g. see Lazrus et al., 1970), lake sediments and peat accumulations are the best evidence for the history and spatial extent of regional atmospheric loading of lead. Many investigators are currently collecting and analysing precipitation samples for lead to determine atmospheric deposition rates. All of these studies unfortunately suffer in that a significant fraction of lead reaching the earth's surface does so as dry deposition, intercepted fog, dew and cloud moisture, all of which are generally not recorded by wet-only collectors (e.g. see Lindberg and Turner, 1983). Studies of wet-only deposition of lead, indicate deposition rates of less than 1 μg cm^{-2} a^{-1} for the northeasternmost US (Maine) (e.g. see Kahl and Norton, 1983).

This paper focusses on the record left in lake sediments and ombrotrophic peat deposits. The conclusions from these data will be compared with studies of soils and the sparse precipitation chemistry data for lead.

Data for this paper were gathered using funding from the US Environmental Protection Agency, Department of the Interior (Fish and Wildlife, National Park Service, Geological Survey), National Science Foundation, Department of Energy and the Electric Power Research Institute (the PIRLA Project). Elaine Hall, Denis W. Hanson, Marilyn Morrison and Geneva Blake, along with many undergraduate and graduate students, assisted in all aspects of these projects. We have profited from many discussions with R.B. Davis and Kimmo Tolonen about lakes, bogs and analysis of data.

Methods

Lake sediment cores are best retrieved with a piston corer (e.g. Davis and Doyle, 1969). Small diameter corers (less than ca. 6 cm) without pistons typically compress the sediment during coring, the effect increasing with sediment depth and decreasing core tube diameter (Hongve and Erlandsen, 1979). The compression reduces apparent accumulation rates for any constituent in the core and alters the chronology if ^{210}Pb dating is used. Large errors can be introduced. Large-diameter pistonless corers (either circular or of the box type) greater than 12-15 cm in diameter probably yield nearly uncompressed sediment but, because of their size, are not nearly as portable and thus cannot be used on remote lakes. Peat cores (0.5-1.0 m long) are typically taken with a simple stainless steel corer. If the core is greater than 20 cm in diameter, little or no compression of peat occurs.

The establishment of the age of successive levels of lake sediment or peat is critical to the establishment of the history of air pollution. The determination of the atmospheric loading rates from lake sediment or peat can be done only by establishing the proportional relationship between atmospheric loading rates and net accumulation rates, which may be greater or less than the former. Prior to 1970, dating for young sediment (less than ~ 200 years old) was accomplished using stratigraphic markers of known age such as pollen horizons, charcoal layers and unique sedimentological events (e.g. ashfalls) or by varves. Pennington et al. (1973) introduced the technique of using ^{137}Cs (a nuclear bomb fall-out nuclide) as a stratigraphic marker with several identifiable ages (e.g. 1954, 1963). Although the technique works and approximately agrees with ^{210}Pb dating in some types of lakes, it frequently fails, largely because of the chemical mobility of ^{137}Cs (Davis et al., 1984; Sholkovitz, 1985). The most accurate methods for dating of lake sediment use the counting of varves or ^{210}Pb. Varves occur in only a small percentage of North American lakes. Varves, if present, enable age resolution of a single year. ^{210}Pb dating (Krishnaswami et al., 1971; Appleby and Oldfield, 1978) enables relatively continuous dating of sediment. However, even with perfect accuracy, resolution of absolute ages is limited by the thickness of sediment intervals which are sampled, coupled with the net sediment accumulation rate (cm a^{-1}). Typically, researchers have sectioned sediment cores in 0.5- or 1.0-cm intervals in lakes with a sedimentation rate of ca. 1 mm a^{-1}. Thus, age resolution under ideal conditions is no worse than 5 or 10 years. The dating technique is not without problems because of both natural processes (such as bioturbation) and analytical errors. A reasonable estimate of the error is probably on the order of 10%. Therefore, sediment dated as 1885 (100 years old) would have an error of about ±10 years. The reliability of the method deteriorates rapidly in sediment more than 100 years old.

Lake sediment ages are based on ^{210}Pb dating. Bulk chemical analysis of lake sediment (Buckley and Cranston, 1971) and determination of water content (heating at 90°C for 24 h) and oxidizable hydrocarbon content (heating at 550°C for 3 h) were conducted on the same aliquot of sediment. The ^{210}Pb dating is typically based on using only about half of the sediment intervals representing the last 100 years, whereas chemistry is based on all intervals. Accumulation rate plots (Figures 1b, 4, 5, 6, 7) are shown with points representing sediment intervals for chemistry, not ^{210}Pb chronological points. Peat chemistry is determined in a similar fashion, except that the water content is determined by heating for about 1 week, at about 40°C, to constant weight. Considerable sediment data in the literature are based on an acid leaching of bulk sediment or peat. Variables in the analytical process include type of acid, temperature and time of leaching, and proportions of acid and solid. Thus the reported lead concentration and not the bulk composition is operationally defined. Consequently, comparisons of the results of different studies are difficult. Recently, attempts have been made to determine different fractions of metals, including lead, in sediment. Samples are subjected to successive extractions, analogous to those used widely in soil science. Although the extractions can be standardized, pre-treatments of sediment (temperature changes, degassing, oxidation, etc.) vary, and operationally defined metal fractions are thus not necessarily comparable from study to study (Rapin et al., 1986).

The weakness of the bulk chemistry approach is that lead derived from the bedrock and soils of the drainage basin cannot be distinguished from other lead (including lead from soil dust (polluted or not) as well as anthropogenically emitted lead). However, in the eastern part of North America, anthropogenic lead fluxes are typically much larger (10-20 times) than natural fluxes. That portion of the lead in the lake sediment which is anthropogenically derived can be approximately determined by normalizing the total lead accumulation rate to that of TiO_2. Titanium dioxide is largely derived from the drainage basin. This normalization technique does not work in ombrogenous peat where the atmospheric flux of lead and TiO_2 is the total flux, and they covary and are comparable.

In both lake sediment and peat, the analyses for lead are most commonly performed with flameless atomic absorption spectrophotometry, as were ours.

Assumptions in Interpretations

The most useful portrayal of information relating to lead is net accumulation rate as a function of time. One would like to be able to transform that rate into an atmospheric loading rate. For this to be possible with lake sediments, we must make certain assumptions:

1) Chronology must be accurate. Given sedimentation rates of about 0.1 cm a^{-1}, resolution is limited to 5-year intervals for which we can calculate average accumulation rates. The precision of chronology is affected by mixing (see 4), below).

2) Sedimentation is continuous. This is probably true for profundal (deep-water) sediment cores.

3) The metal of interest (lead) has low chemical mobility so that, if chemical conditions change, lead does not diffuse after primary deposition.

4) After lead is deposited in a stratum, vertical mechanical mobility should be non-existent. This process would relocate lead in older or younger sediment, changing apparent deposition rates. The condition of no mechanical mixing is found only in lakes with laminated sediments which are relatively rare in the eastern US and Canada. However, most deep oligotrophic lakes have minimal mixing of profundal sediment. Fortunately, the degree of mixing can be approximately determined, and unsatisfactory stratigraphic records can be rejected.

5) Transport of lead from the terrestrial watershed to the lake is generally believed to be minor, typically less than 5%. For example, Friedland and Johnson (1985) found that only 1-2% of the lead falling on the terrestrial area in a year reaches the lake. However, sediment can be redistributed from shallower to deeper water with an associated increase in the accumulation rate at the site of the coring. This is called sediment focussing. As long as this process is steady-state, trends in sediment accumulation rates may partially reflect trends in atmospheric deposition rates. It is likely that the concentration of lead in sediment deposited early in the pollution history is diluted by older sediment containing little anthropogenic

lead. Recent declines in atmospheric lead and recent sediment may not be reflected by parallel changes in the accumulation rate because of dilution by lead-rich sediment. Thus a hysteresis effect may operate. Furthermore, some lakes have very high flushing rates. In such lakes, sediment accumulation rates are low, and inferred atmospheric deposition rates will be underestimated.

6) Background lead accumulation rates (pre-industry, pre-1850) range from about 0.1 to 1.0 $\mu g\ cm^{-2}\ a^{-1}$. Our ability to identify the earliest signal relating to atmospheric deposition of lead will relate to the signal-to-noise ratio. It is assumed that background (autochthonous) lead covaries with TiO_2.

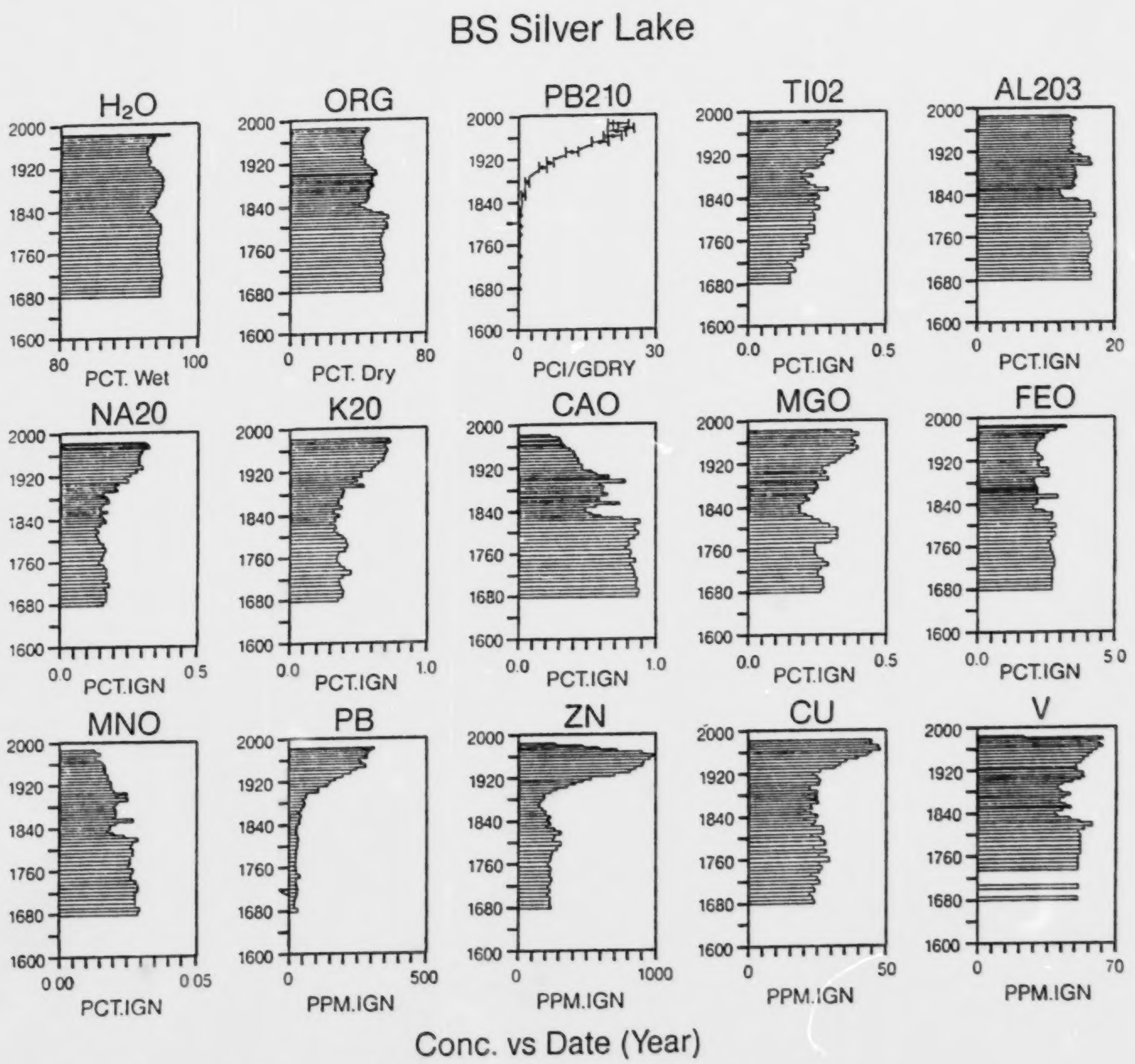
Results

Figure 1a shows the chemistry of a sediment core from Silver Lake, located in the Adirondack Mountains, NY. (Norton, 1984). The profiles for the heavy metals are typical for oligotrophic lakes, with undisturbed watersheds, in the northeastern United States. Lead characteristically increases in concentration in an exponential fashion, starting in the mid- or late-1800s. Most concentration profiles show a maximum in near-recent sediment, with a slight decline over the last 0-15 years (Table 1), depending on the lake. The change in lead accumulation rates in recent sediment is attributed to a decline in the use of tetraethyllead in gasoline. The net accumulation rate (Figure 1b) is also characteristic, with a typical background and peak value. From a consideration of Table 1 and Figures 1 and 2, it is unlikely that the concentration of lead in lake sediments, or accumulation rates derived from it, directly reflects the atmospheric deposition rate. It is likely that trends in atmospheric deposition are reflected by proportional changes in

Table 1.

Accumulation of Pb for 10 lakes in the Adirondack Mountains, NY (from Norton, unpublished).

	Pb Concentration ($\mu g\ g^{-1}$)			Ratio,	Pb Deposition Rate ($\mu g\ cm^{-2}\ a^{-1}$)			Ratio,
Lake	Background	Maximum	Year of Max.	Maximum Background	Background	Maximum	Year of Max.	Maximum Background
Brooktrout	27	558	1982	21	0.14	2.06	1968	15
Deep	25	640	1973	14	0.06	2.01	1973	34
Fourth	15	270	1976	18	0.10	2.55	1976	26
Jerseyfield	26	675	1979	26	0.12	3.42	1979	29
Merriam	20	459	1980	23	0.07	3.70	1980	53
Panther	40	498	1967	12	0.25	5.5	1981	22
Sagamore	65	335	1979	5	0.8	4.82	1983	6
(BS) Silver	26	307	1978	12	0.12	2.50	1980	21
T	37	299	1982	8	0.16	2.54	1974	16
Upper Wallface	24	759	1979	32	0.09	3.36	1979	37



BS Silver Lake

Conc. vs Date (Year)

Figure 1a Sediment Chemistry from a Core Silver Lake, Adirondack Mountains, New York.

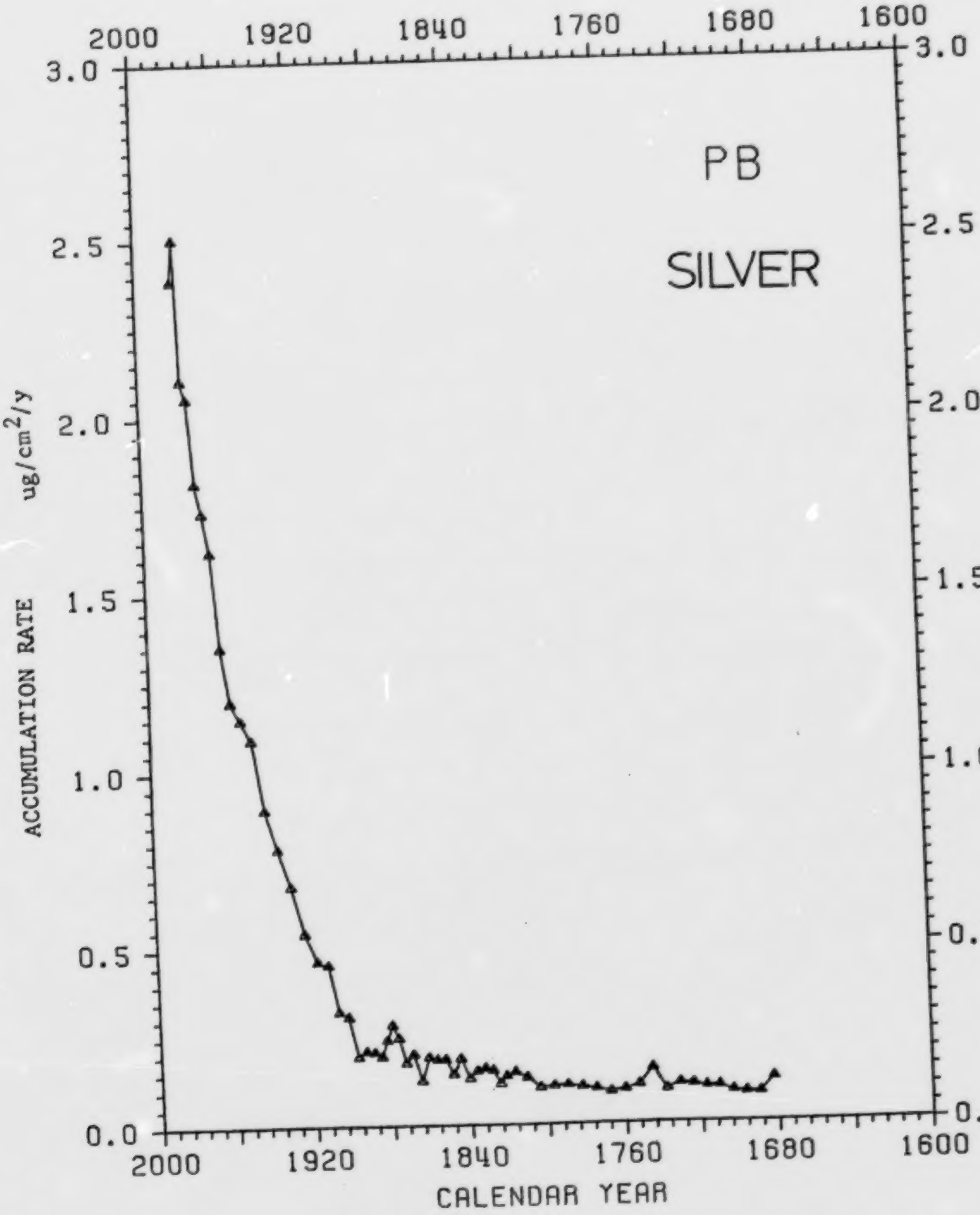


Figure 1b. Net Accumulation Rate for Lead for the Core in Figure 1a.

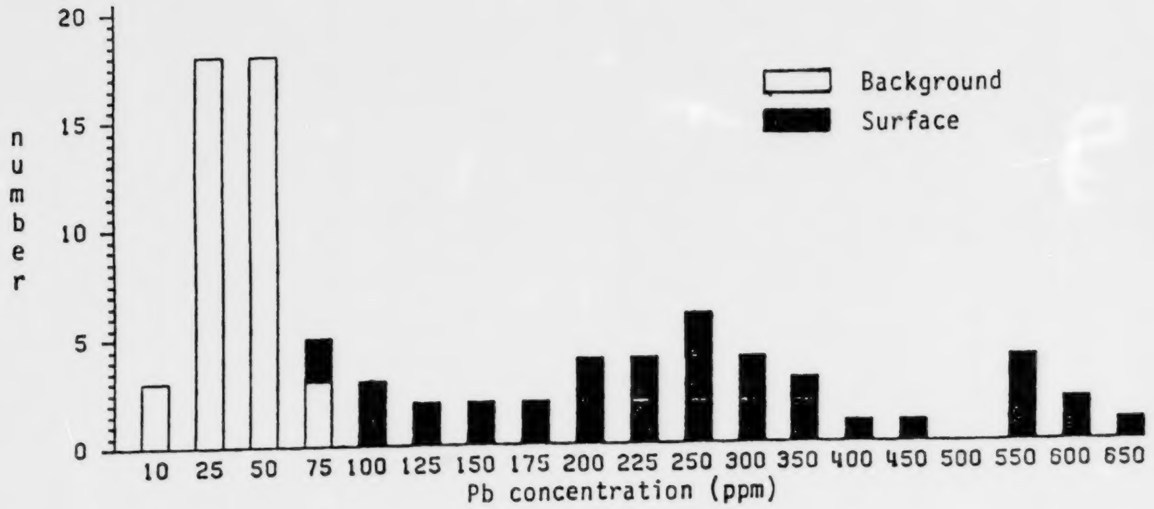


Figure 2. Background (pre-industrial) Lead Concentration Versus that of Surface (0 - 1.0 cm) Sediment for Lakes in New England and New York.

lead accumulation rates in lake sediment, modified by resuspension and deposition of older sediment.

Dillon and Evans (1982) evaluated the whole-lake burden of anthropogenic lead. They demonstrated the spatial variability of concentration (and accumulation rate) profiles in a lake basin. The PIRLA project (Charles et al., 1985) evaluated the representativeness of a single core taken from the profundal area of the lake. Figure 3a, b and c shows the chemical profiles for lead for three cores from McNearney Lake, MI, taken in close proximity to each other (ca. 5-10 m horizontal separation). Their similarity (and that of derived accumulation rates for all metals) suggests that a single core from the profundal area is generally representative of sediment in that portion of the lake. Similar conclusions have been reached from studies of sediment from Big Moose Lake, NY, Mud Pond, ME, and Haystack Pond, VT (Norton, Charles, Whitehead and Davis, unpublished).

Figure 4a, b and c illustrates the risk of assuming that the sediment record from a lake (or bog) is representative of a small region. Little Long, Long and Sargent Mountain Ponds (ME) are within 40 km of each other, and thus receive nearly the same amount and quality of precipitation. However, the sediment profiles for lead are very different, probably because of differing flushing rates and focussing. Similar conclusions can be reached based on the value of the integrated unsupported ^{210}Pb in the sediment (Davis et al., 1984).

Regional variation of lead deposition from the atmosphere and accumulation in sediments is partially masked by limnological characteristics. Figure 5a-e shows lead accumulation rates in sediment for widely separated lakes. Of the five lakes, only McNearney (Figure 5a) is in a relatively 'clean' area (low estimated SO_4^{2-} deposition). The others do not align themselves with any

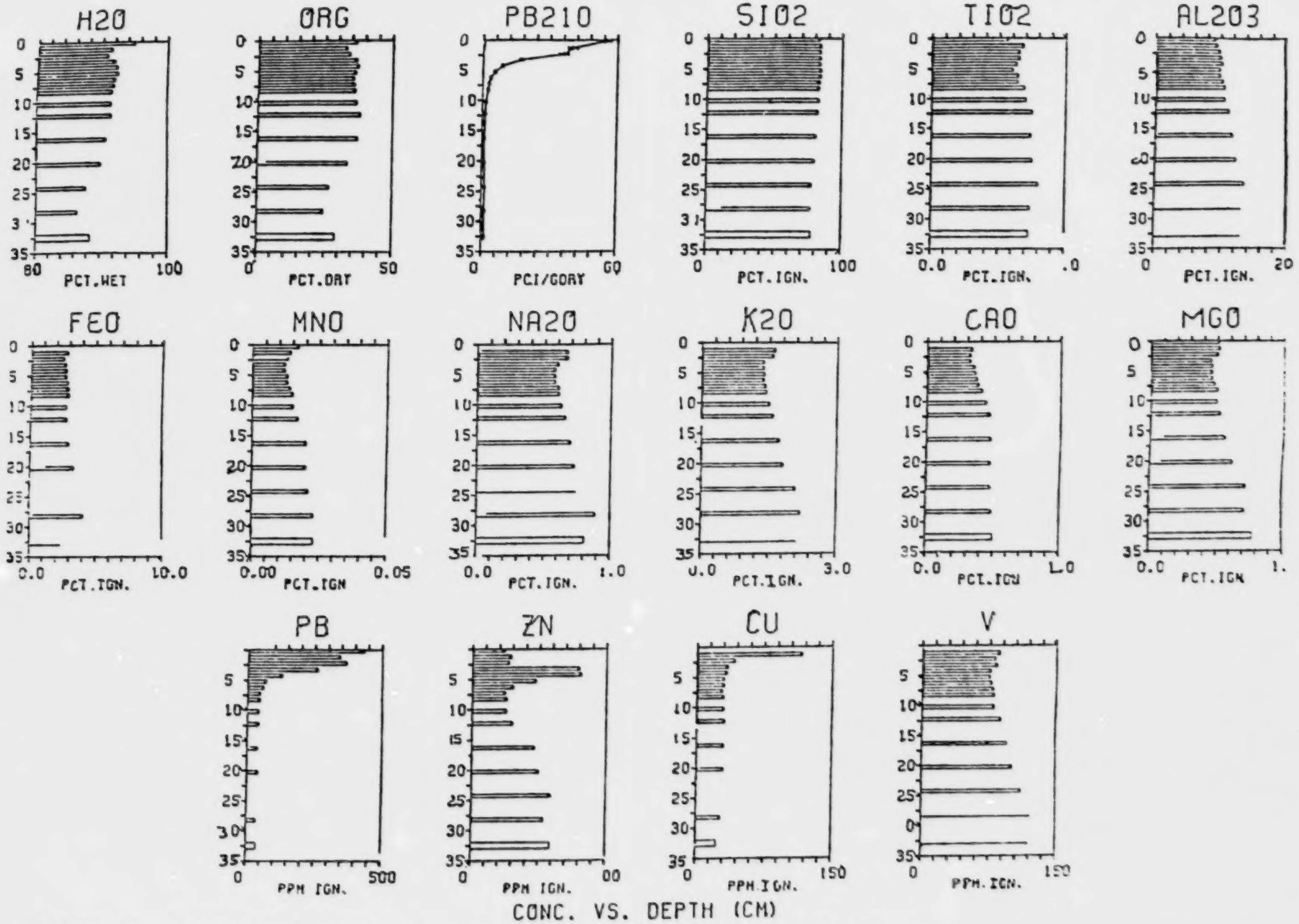


Figure 3a. Sediment Chemistry from Three Cores from McNearney Lake, Michigan.

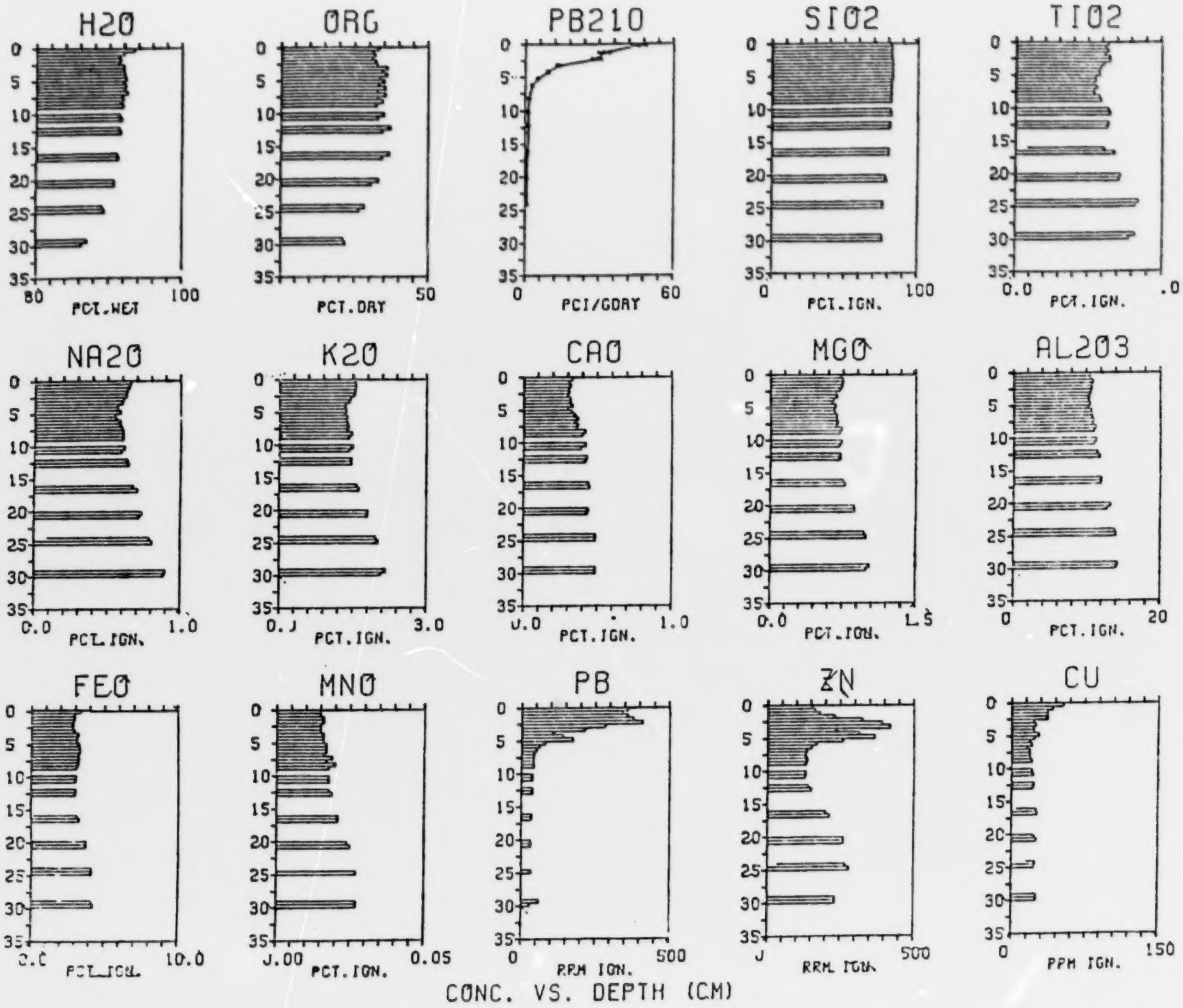


Figure 3b. Sediment Chemistry from Three Cores from McNearney Lake, Michigan.

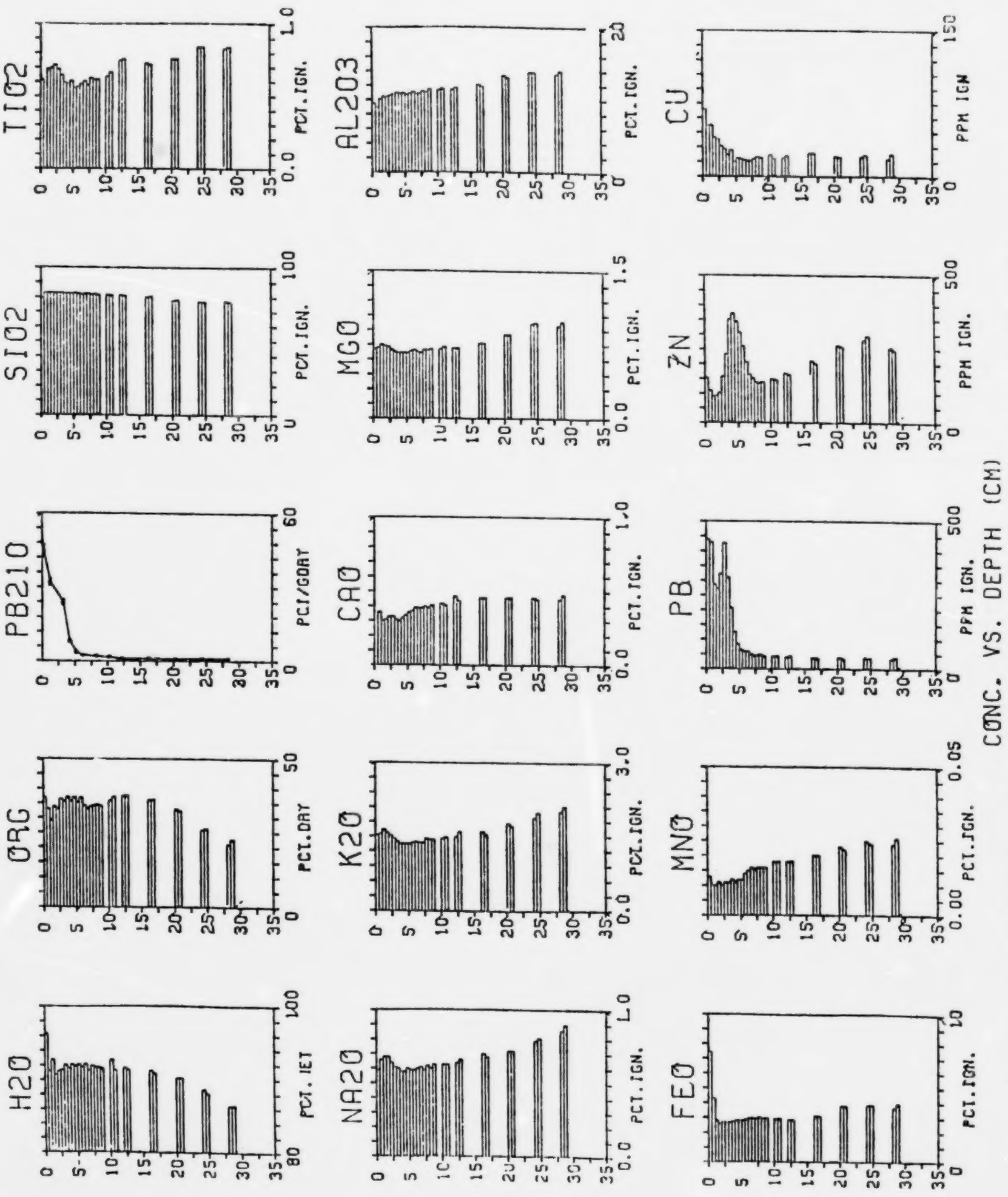


Figure 3c. Sediment Chemistry from Three Cores from McNearney Lake, Michigan.

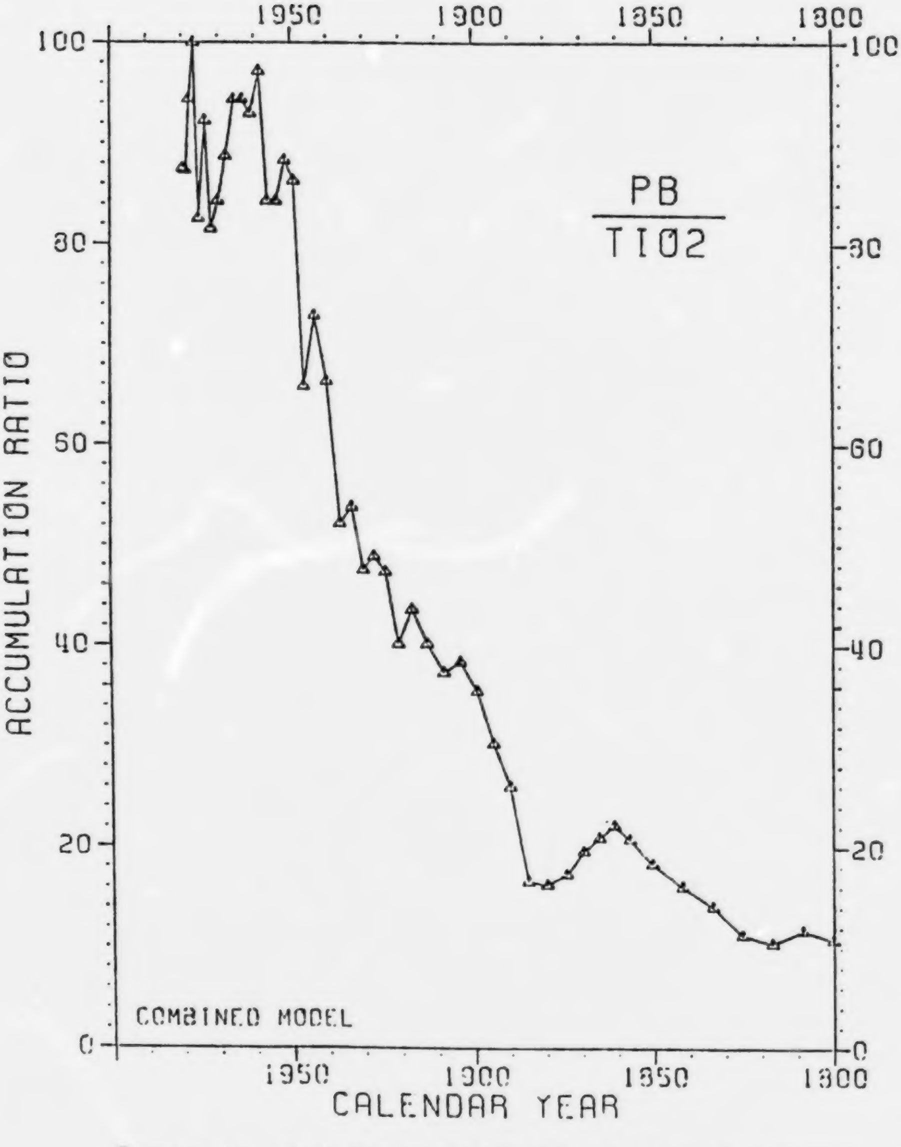


Figure 4a. Net Accumulation Rate Ratios in Sediment Cores from Little Long Pond 24M.

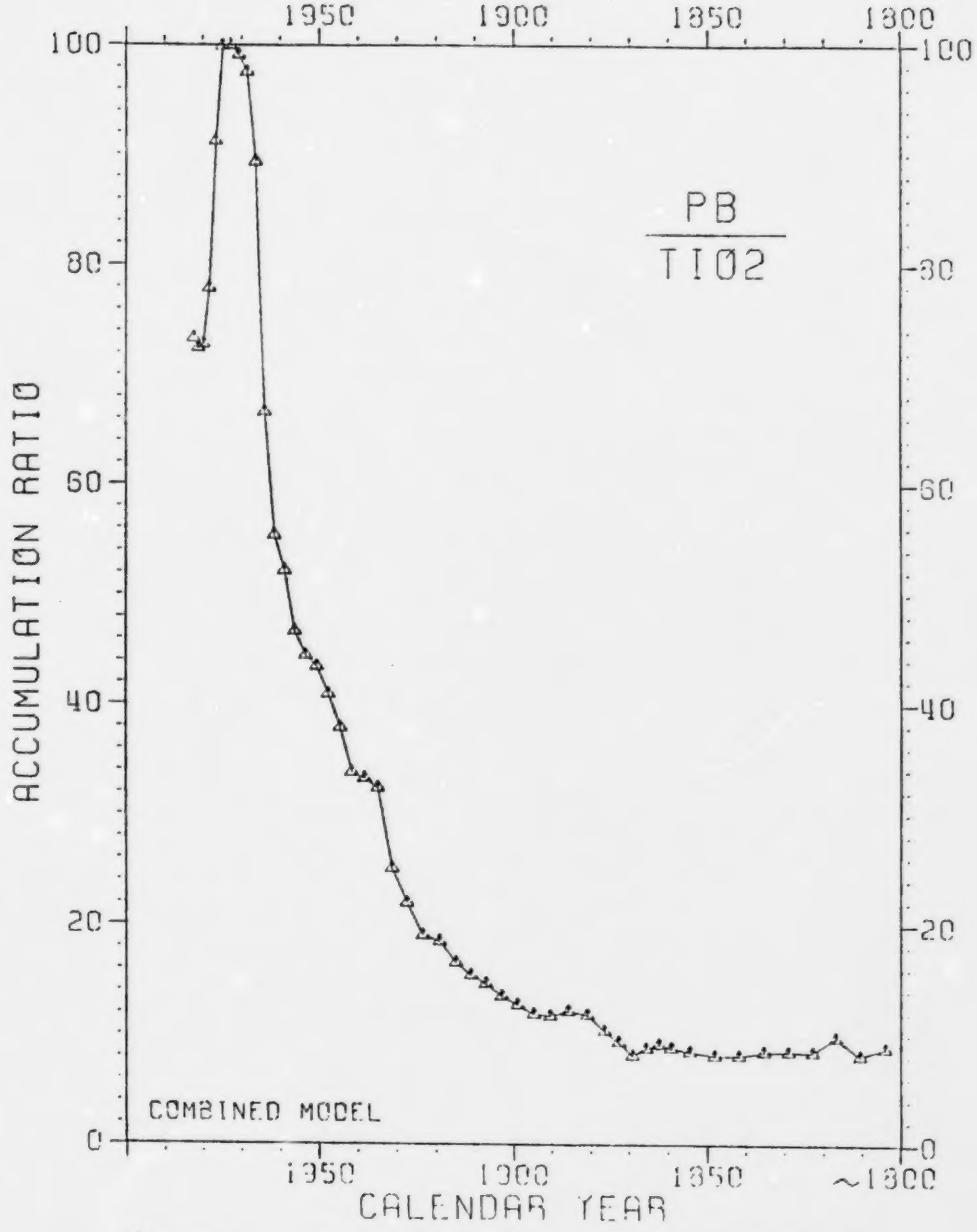


Figure 4b. Net Accumulation Rate Ratios in Sediment
Cores from Long Pond - Isle Au Haut.

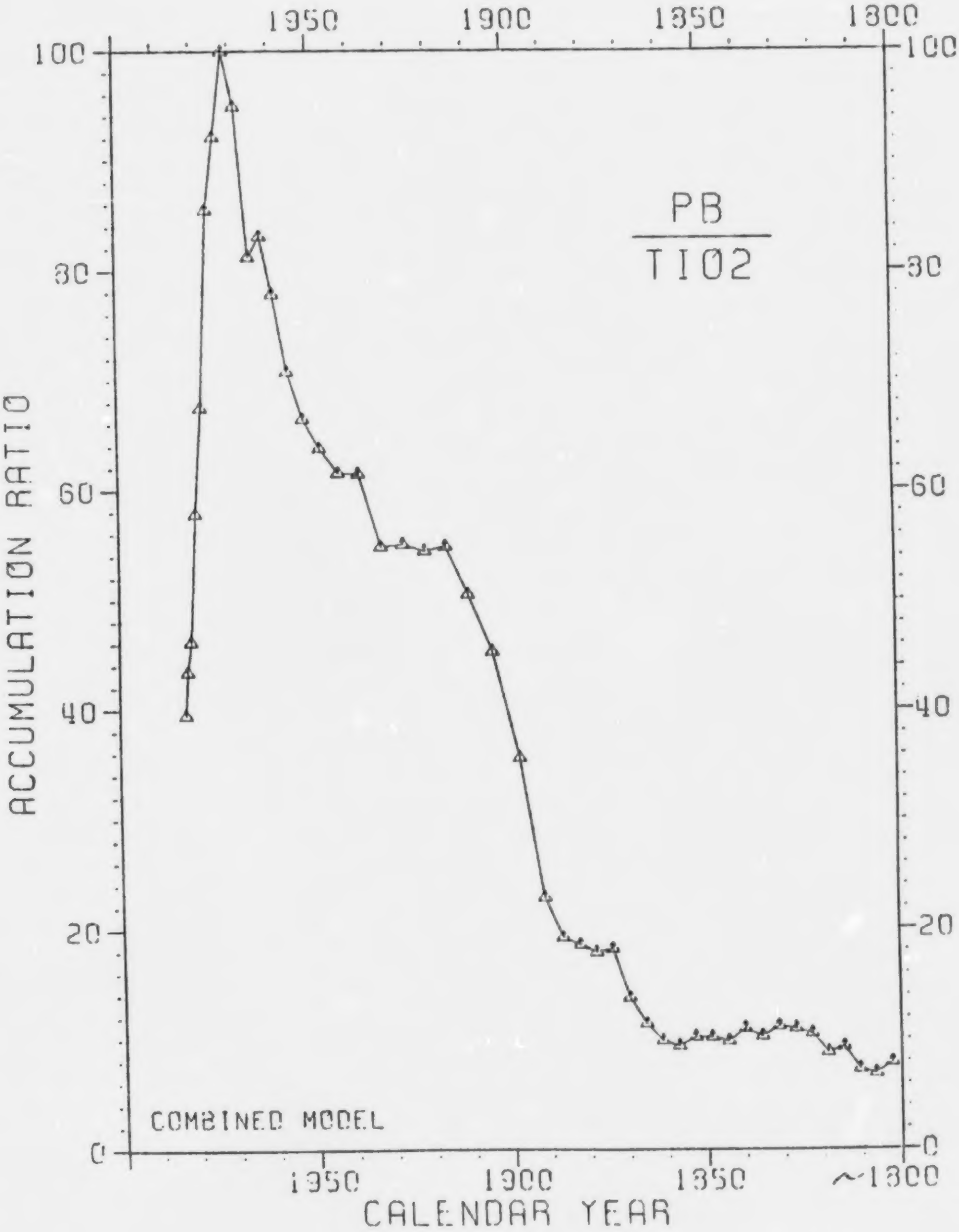


Figure 4c. Net Accumulation Rate Ratios in Sediment Cores from Sargent Mountain Ponds.

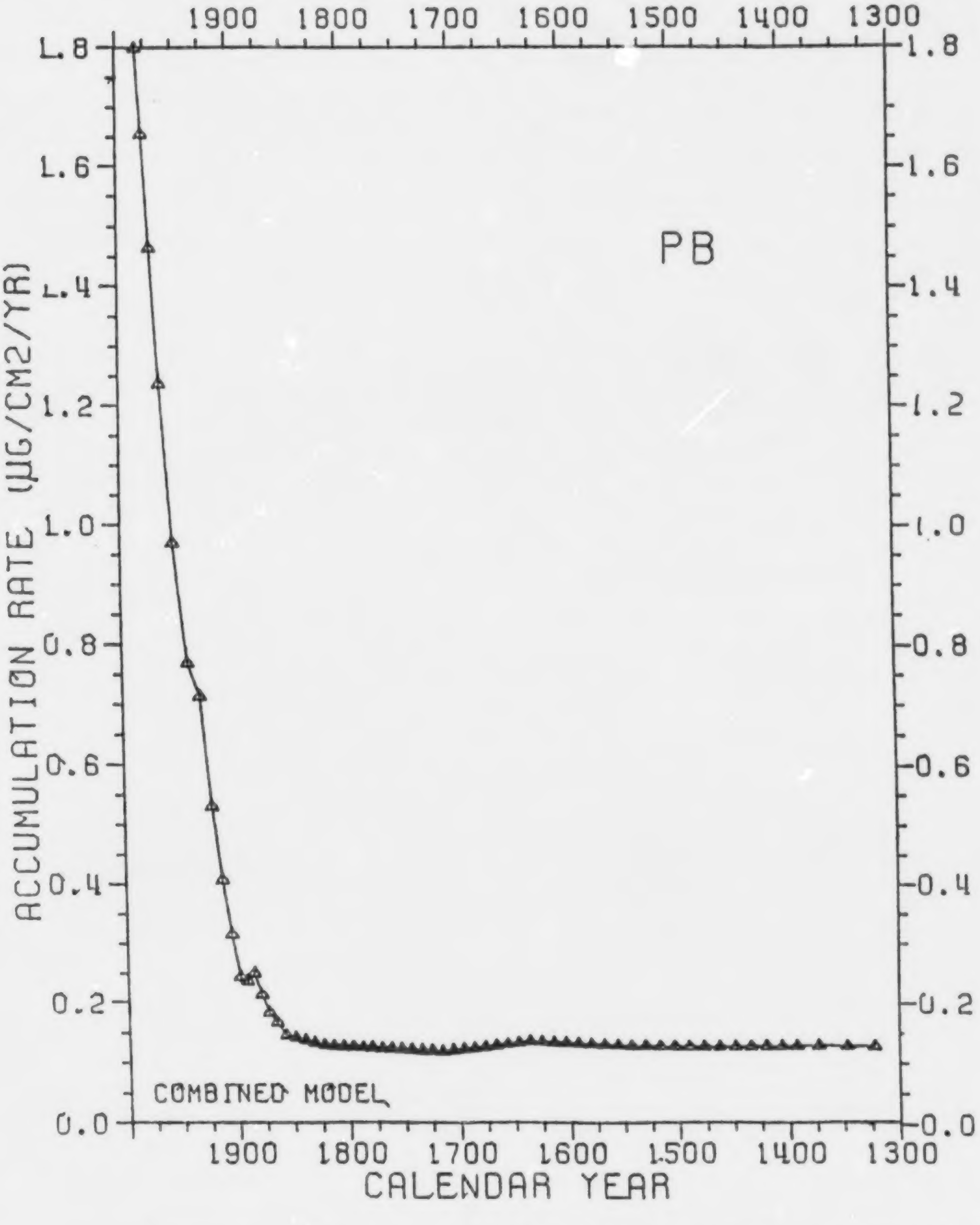


Figure 5a. Net Accumulation Rates of Lead for a Sediment Core from McNearney Lake, Michigan.

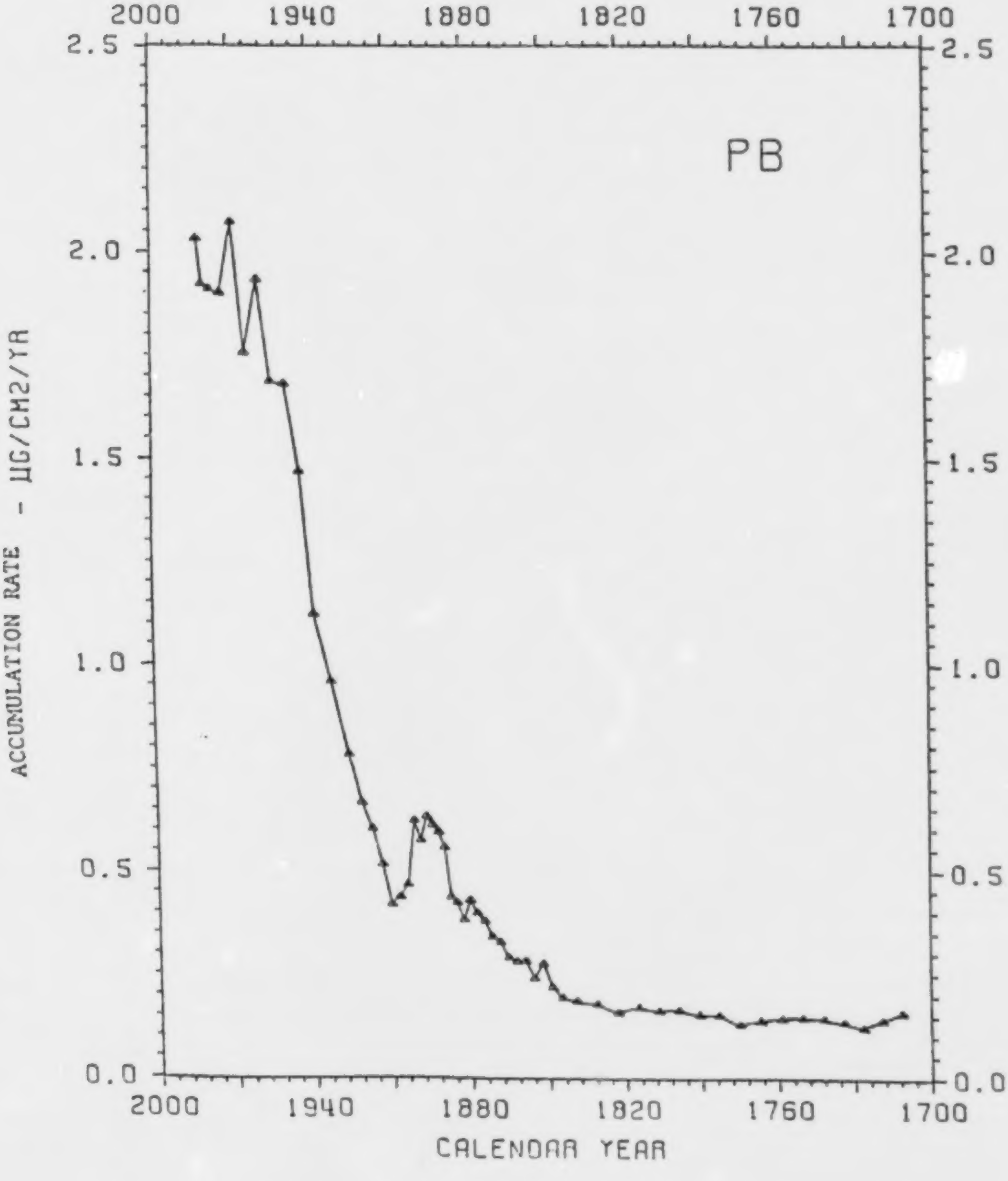


Figure 5b. Net Accumulation Rates of Lead for a Sediment Core from Brooktrout Lake, New York.

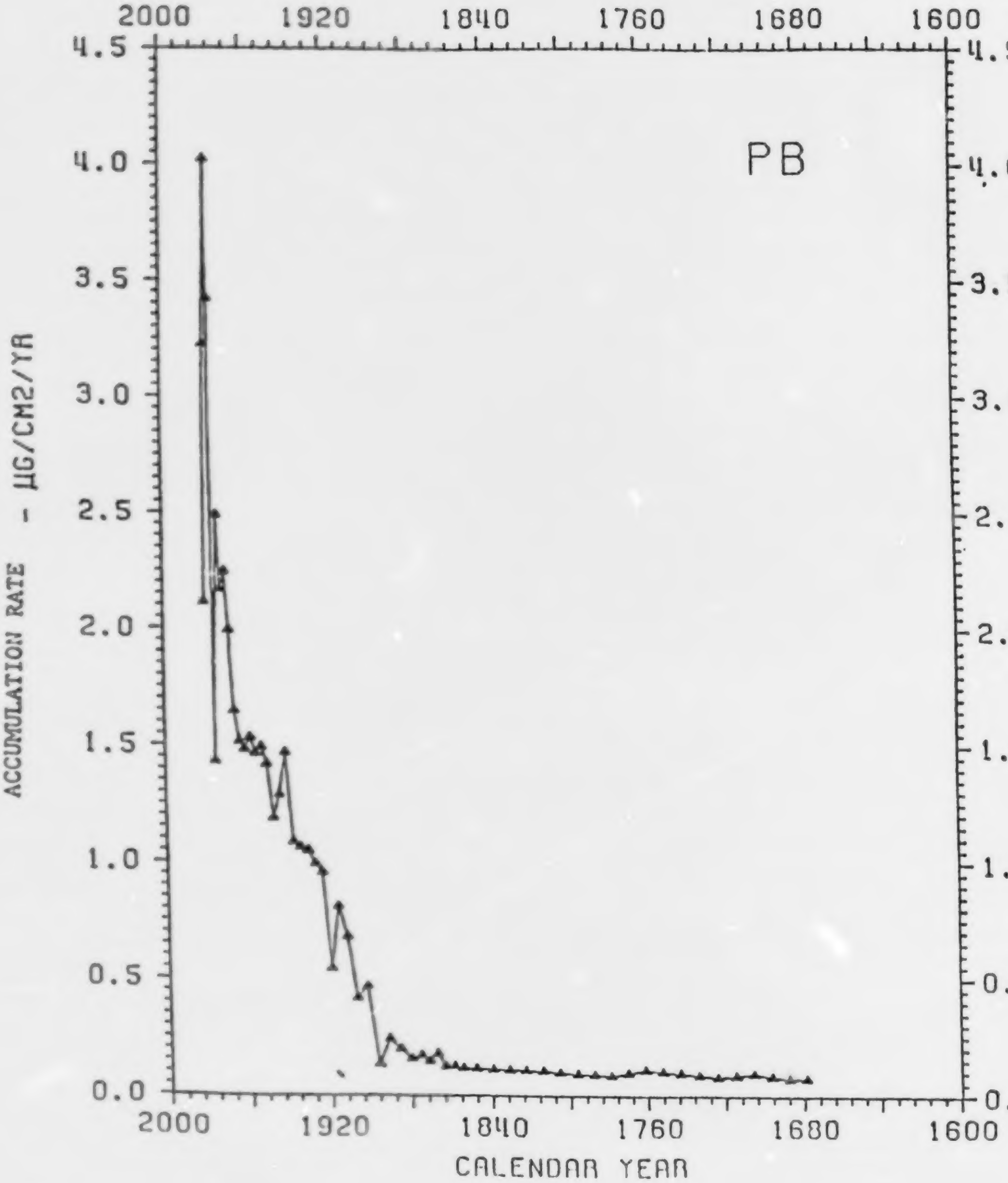


Figure 5c. Net Accumulation Rates of Lead for a Sediment Core from Branch Lake, Vermont.

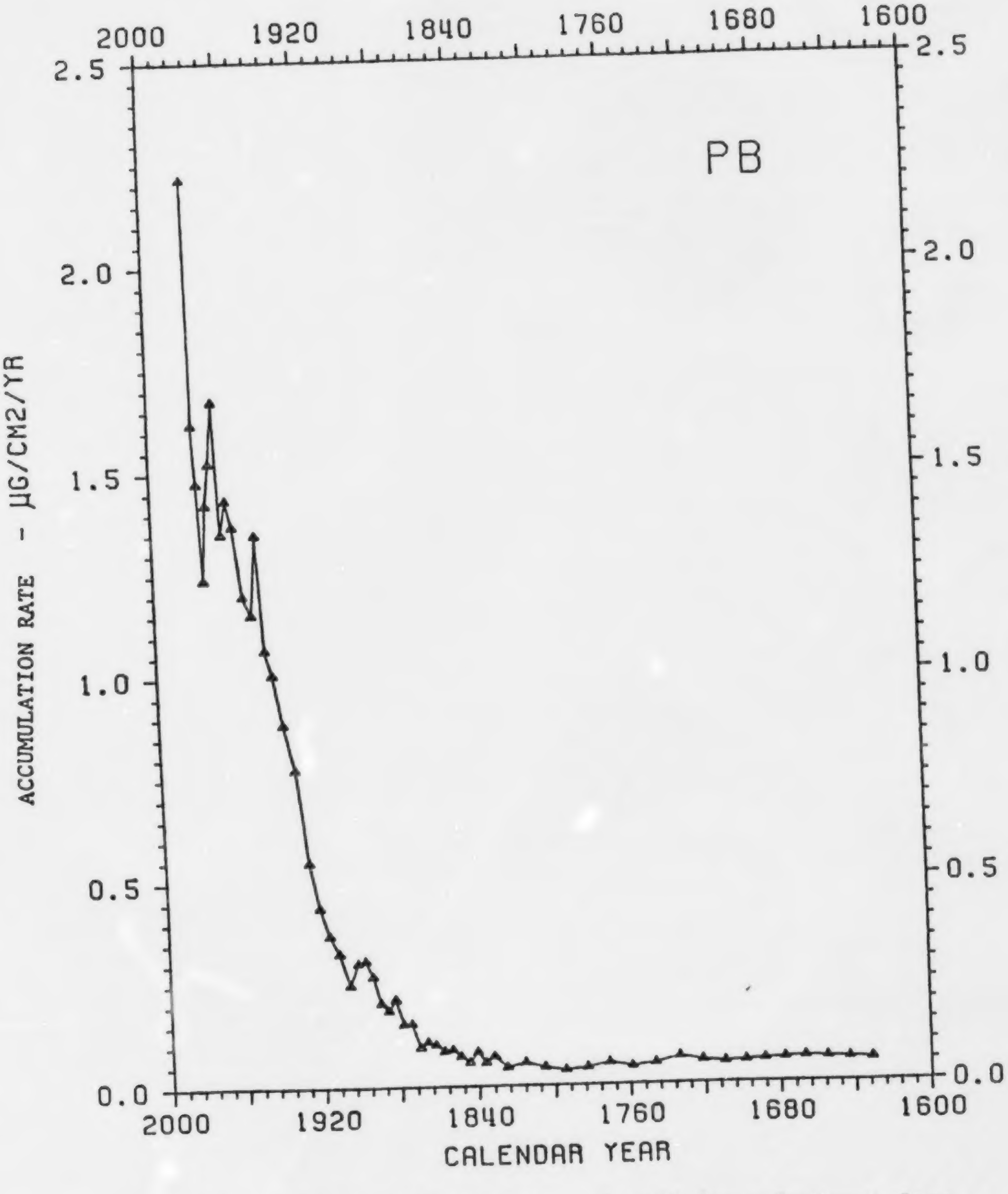


Figure 5d. Net Accumulation Rates of Lead for a Sediment Core from Solitude Pond, New Hampshire.

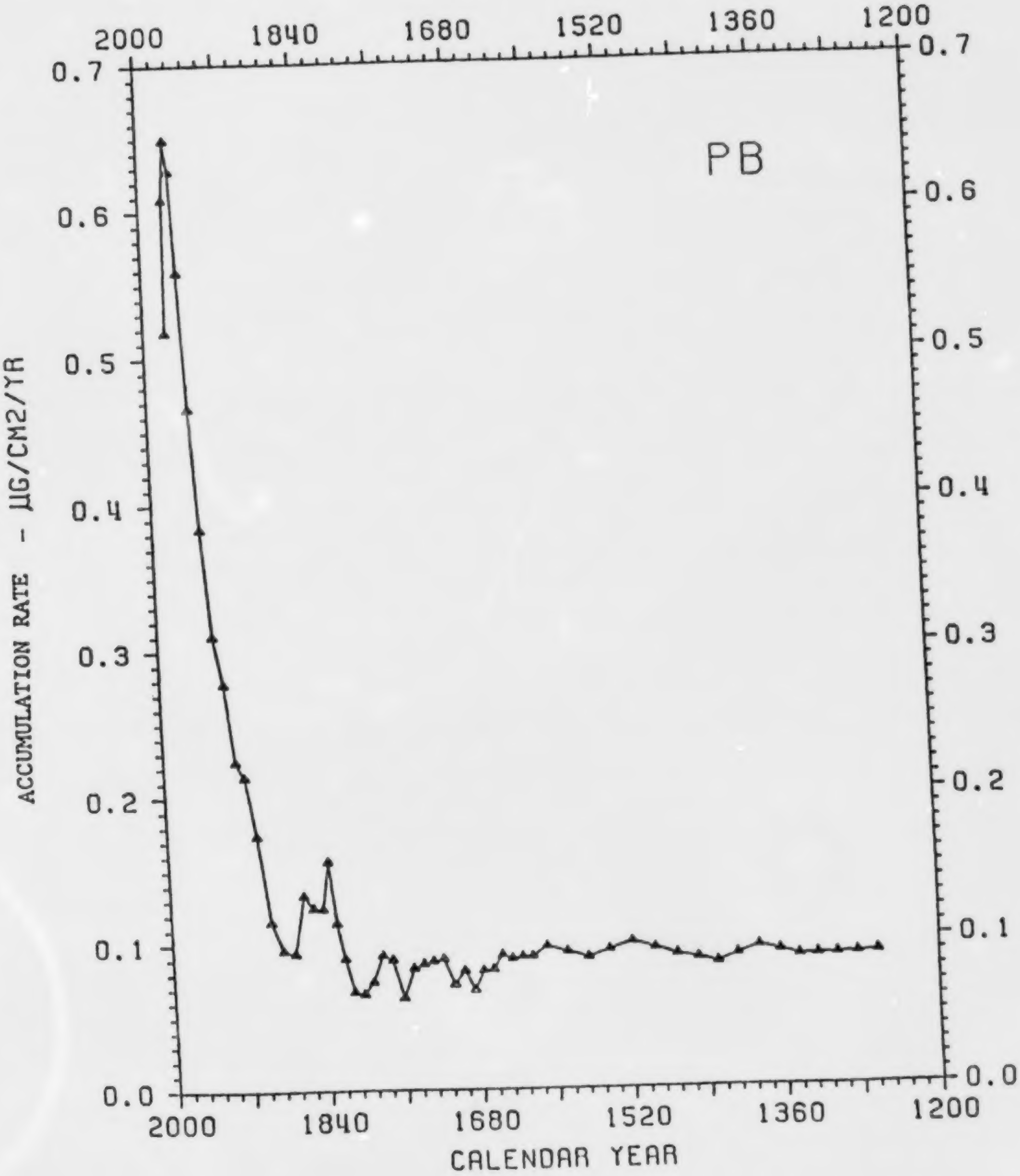


Figure 5e. Net Accumulation Rates of Lead for a Sediment Core from Ledge Pond, Maine.

obvious relationship to precipitation chemistry. One lake apparently cannot give a precise estimate of the regional atmospheric deposition rate for lead, even if lead deposition is correlated with SO_4^{2-} deposition. Source terms and transportation apparently differ.

Lead may be emitted to the atmosphere from a variety of sources including fossil fuel combustion, smelting and the use of leaded gasoline. Figure 6a-d shows the sediment accumulation rate for lead from four high-altitude, remote lakes in Rocky Mountain National Park, Colorado, which do not receive significantly polluted precipitation as indicated by US National Atmospheric Deposition Program data. These data do not, however, include measurements of lead. The sharply increased sediment accumulation rate for lead over the last 100 years is interpreted to be caused by a long period of emissions of lead related to the mining industry of the region. Other elements associated with fossil fuel burning (e.g. zinc) do not increase in the chemical profiles of sediment from these remote lakes. Even though modern emissions of mining-related lead may be reduced, resuspension and redistribution of sediments rich in lead may maintain high net accumulation rates in deep-water sediments as indicated for these lakes.

Figure 7 shows the chemistry (a and b) and accumulation rates (c and d) for lead from peat cores from a hummock and hollow, respectively, from Big Heath, Mt. Desert Island, ME. Although the hummock and hollow profiles yield different lead accumulation rates, they are similar in timing and trend and not substantially different from profiles from sediment from nearby lakes (Norton and Kahl, 1986). The cause(s) of the differing accumulation rates for adjacent hummocks and hollows is not understood. Possible explanations include dating errors, differential dry deposition at the two types of sites,

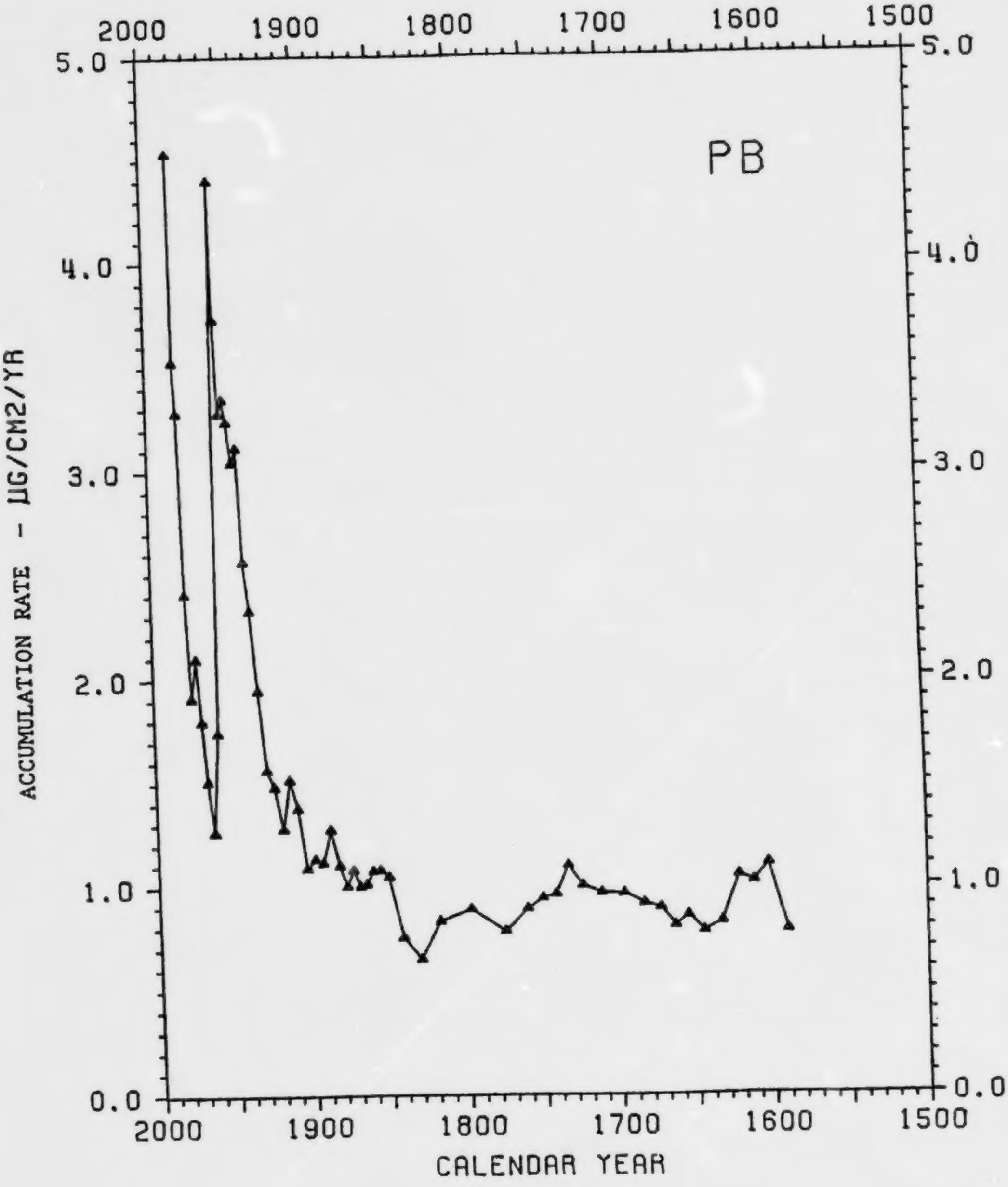


Figure 6a. Net Accumulation Rate Profiles of Lead for a Sediment Core from Emerald Lake, Rocky Mountain National Park, Colorado.

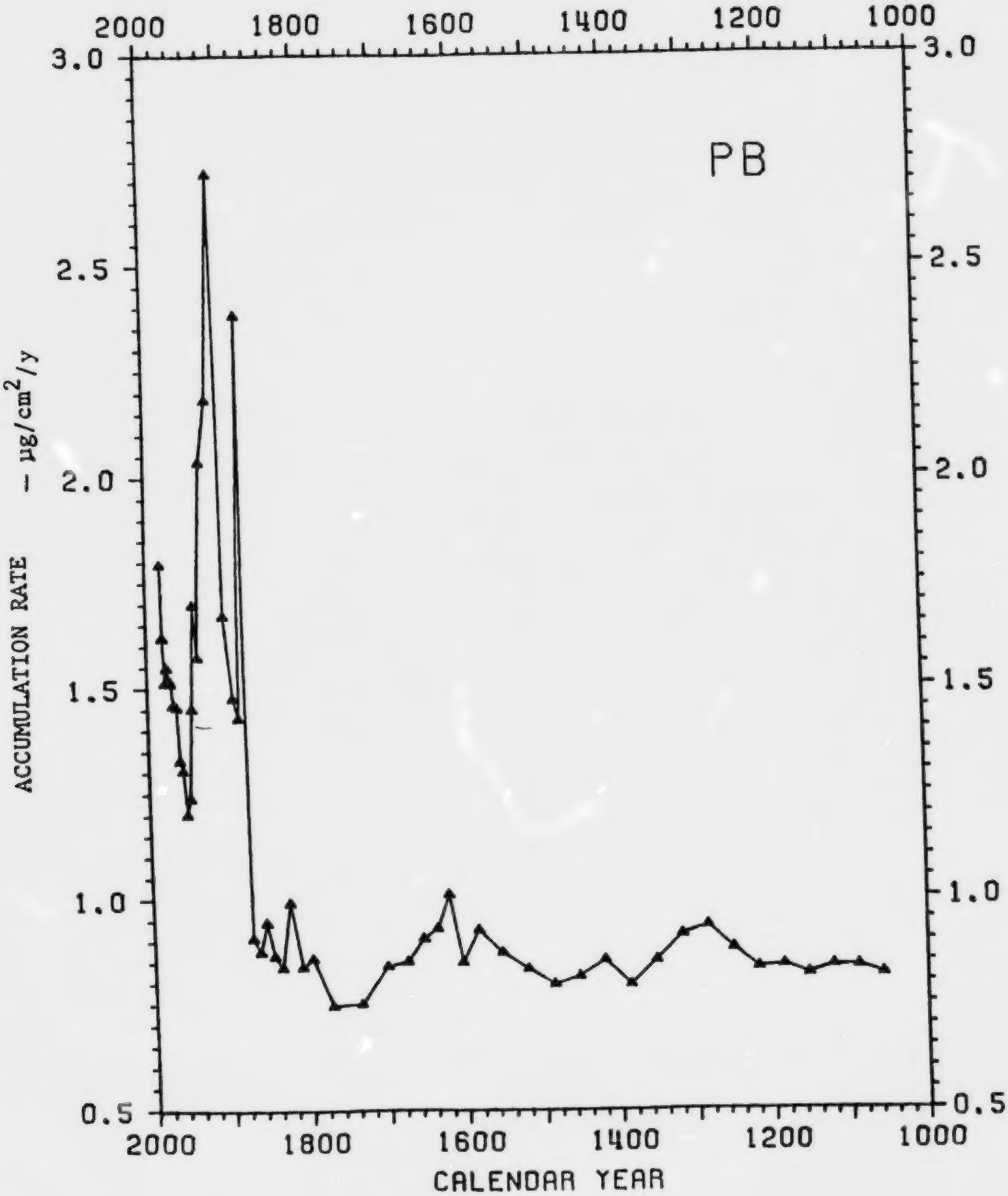


Figure 6b. Net Accumulation Rate Profiles of Lead for Haiyaha Lake, Rocky Mountain National Park, Colorado.

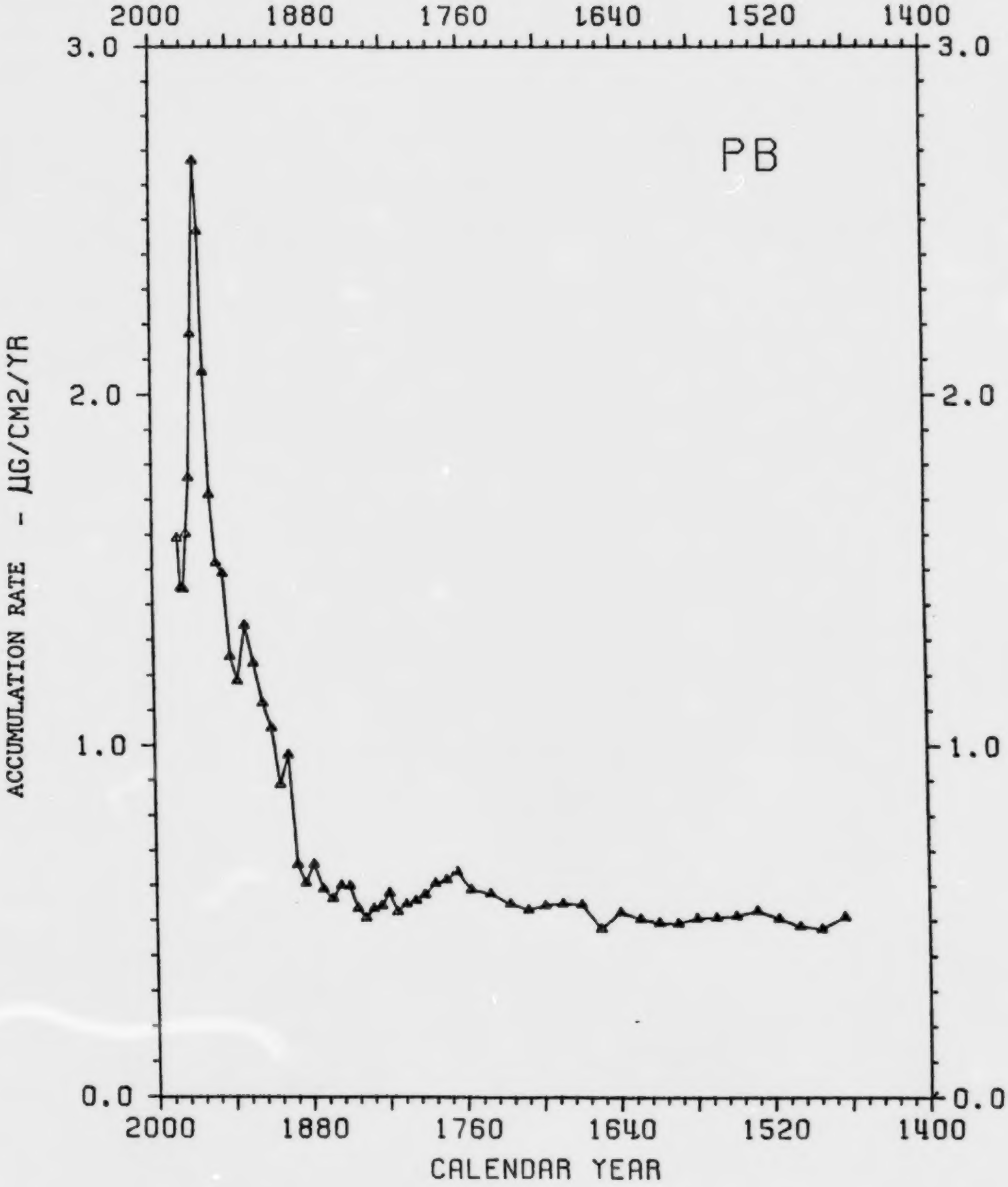


Figure 6c. Net Accumulation Rate Profiles of Lead for Husted Lake, Rocky Mountain National Park, Colorado.

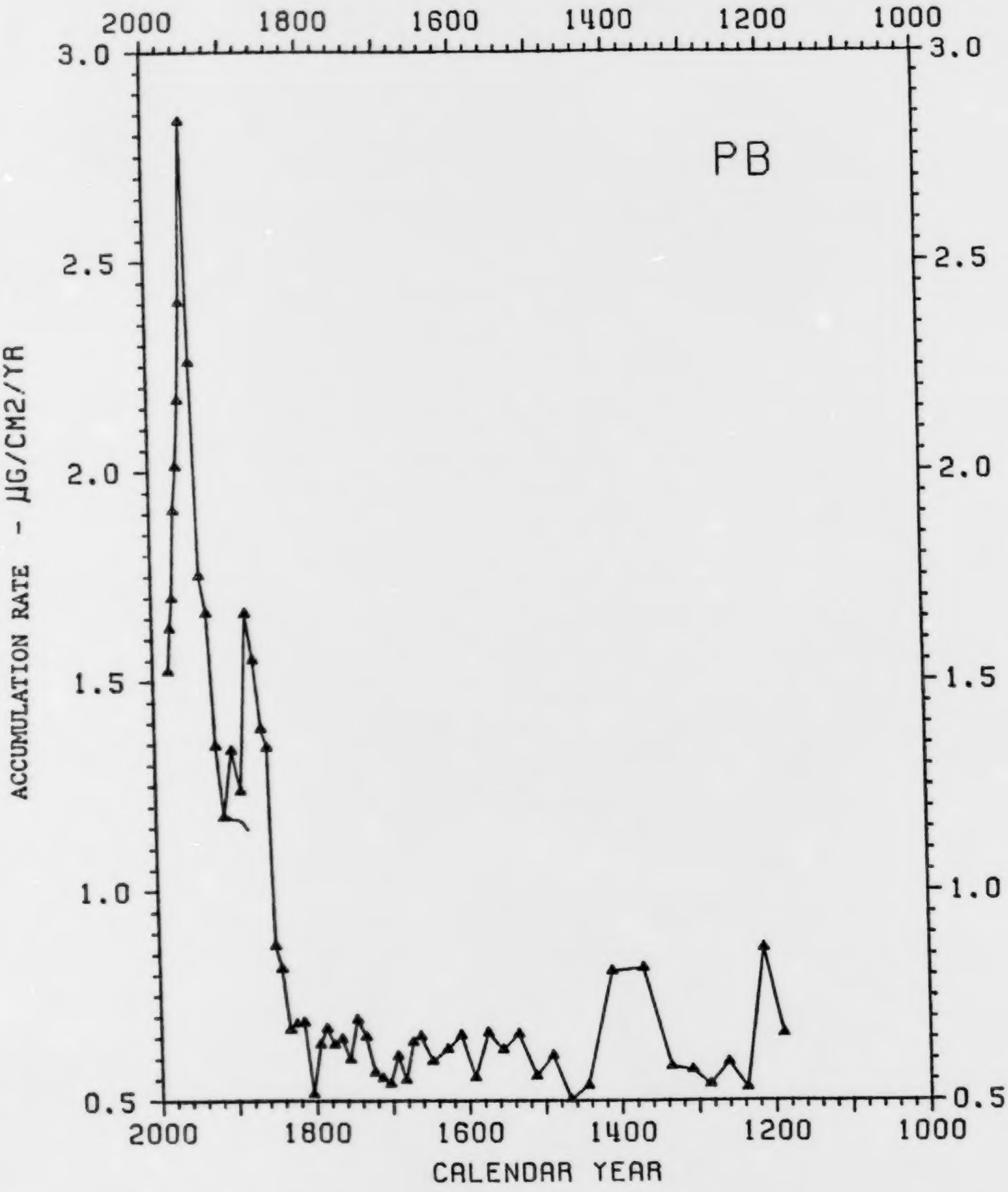


Figure 6d. Net Accumulation Rate Profiles of Lead for Louise Lake, Rocky Mountain National Park, Colorado.

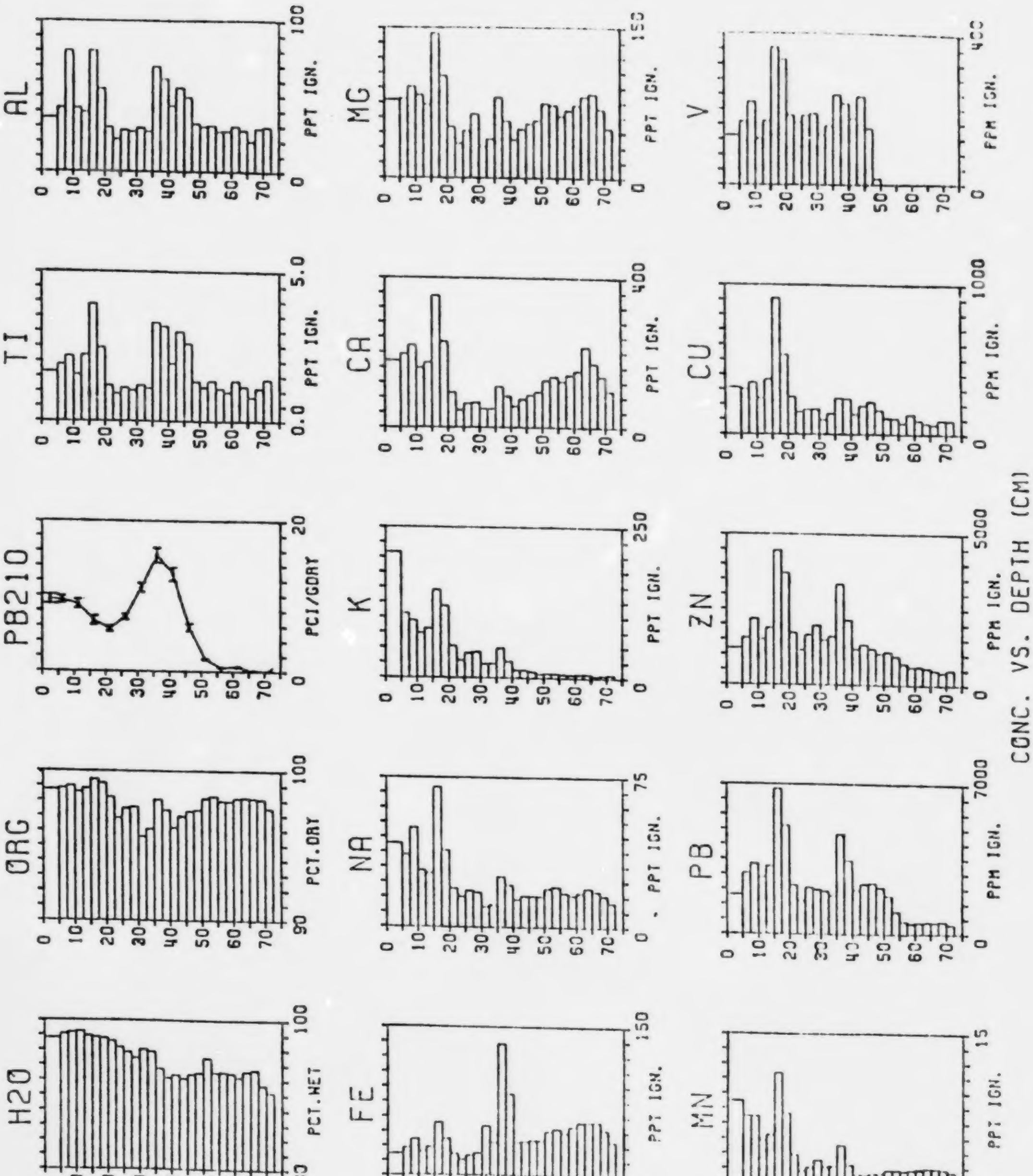


Figure 7a. Peat Chemistry for a Hummock from Big Heath, Mt. Desert Island, Maine.

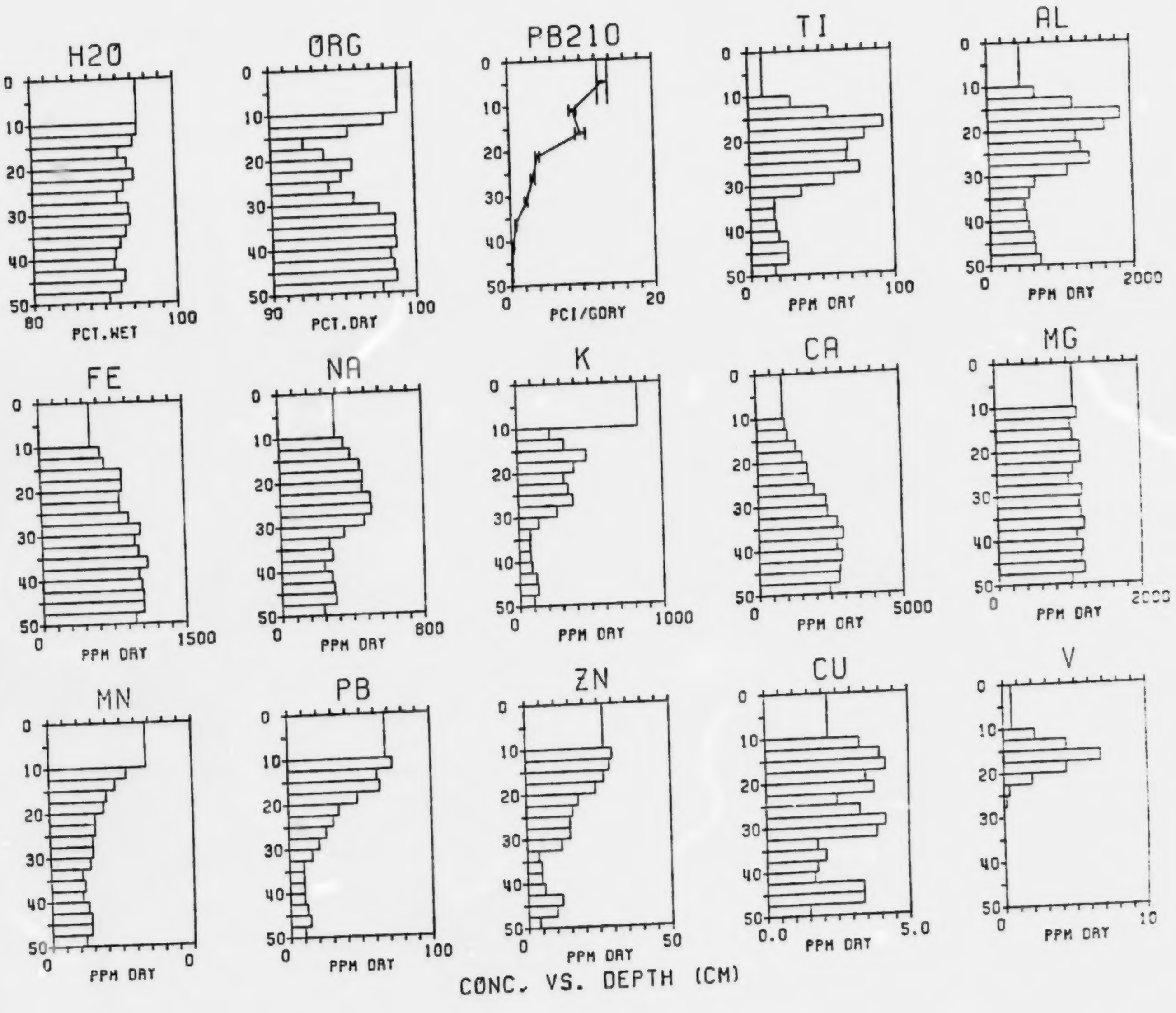


Figure 7b. Peat Chemistry for a Hollow from Big Heath, Mt. Desert Island, Maine.

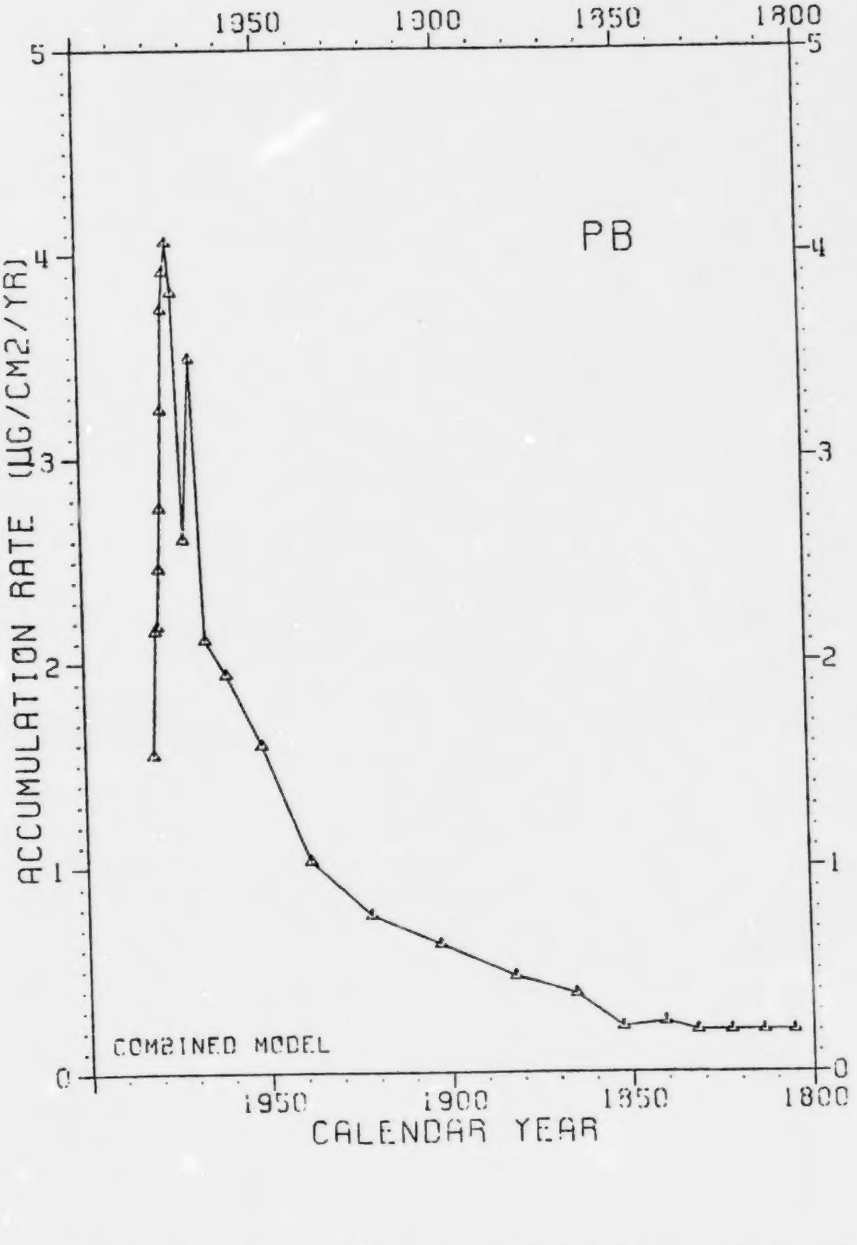


Figure 7c. Net Accumulation Rates for Lead for a Hummock from Big Heath, Mt. Desert Island, Maine.

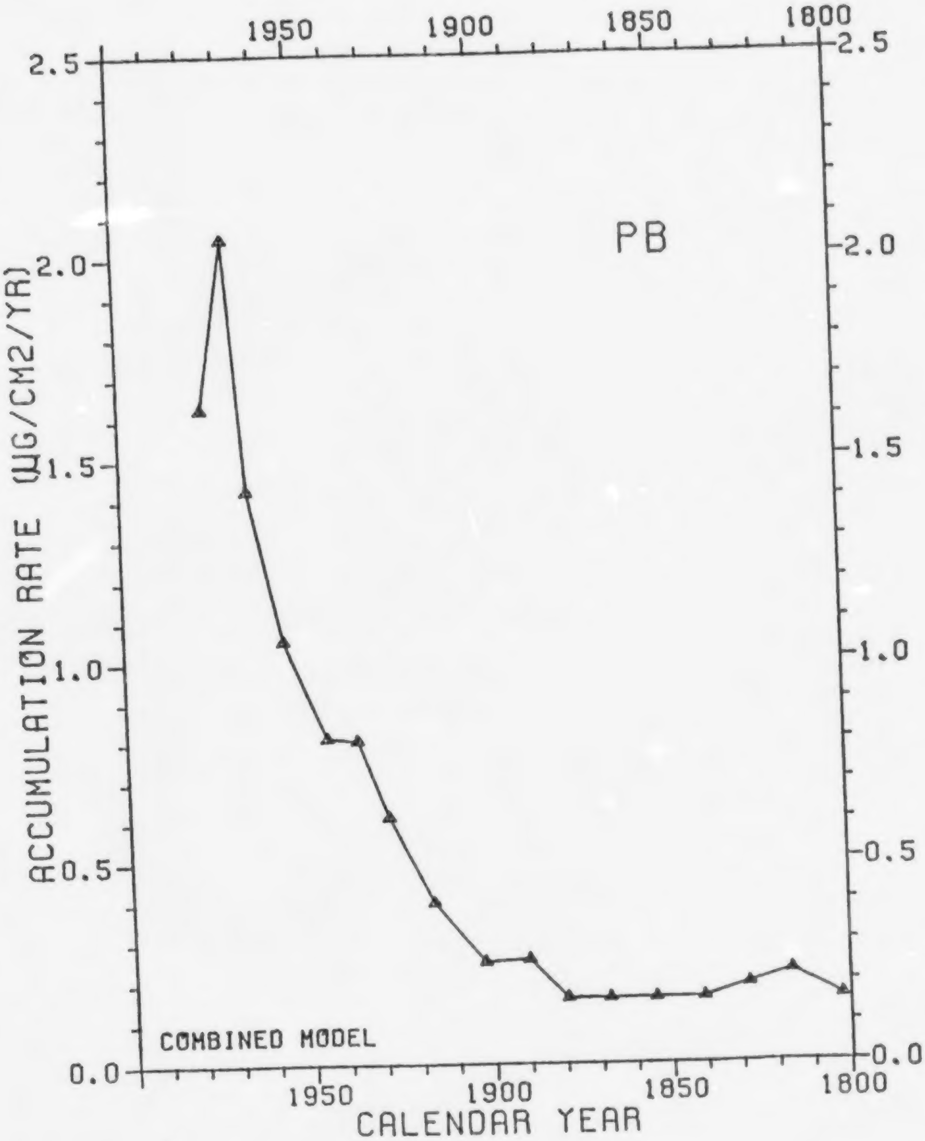


Figure 7d. Net Accumulation Rates for Lead for a Hollow from Big Heath, Mt. Desert Island, Maine.

horizontal and vertical migration of lead from hollows to hummocks and/or preferential loss of lead from hollows.

Conclusions

1) Lake sediment and peat records indicate at least 100 years of elevated atmospheric deposition of lead, with values increasing until the 1970s.

2) Lake-to-lake variations in net accumulation rates for lead preclude using a single core from one lake to reconstruct atmospheric deposition rates. Trends are roughly parallel from lake to lake.

3) Net accumulation rates for lead in lakes, as indicated by single cores, yield values similar to those obtained from nearby peat bogs or historic studies of lead accumulation in soils. All of these values generally exceed loading rates as measured by wet-only deposition. This suggests that dry-fall, fog and cloud moisture are important source terms for lead loading. Total loading would depend on the type of receptors, with lake surfaces receiving the least lead of lakes, bogs and forested systems.

4) Maximum net accumulation rates in New York and New England range from about 1 to 4 $\mu g\ cm^{-2}\ a^{-1}$. Data are not sufficiently well distributed to assess regional variability; interlake variability is too large.

5) Single cores are representative for the area of the lake which is cored but may misestimate total lake loading, and accumulation rates in most cases cannot generally be equated with atmospheric loading.

6) Because of post-depositional processes, the trends in concentration of lead in sediment probably lag behind trends in atmospheric deposition, the amount of lag varying from lake to lake.

7) Multiple emission sources of lead are indicated and include ore mining/smelting, fossil fuel combustion (principally coal) and tetraethyllead

utilization in automotive fuel.

8) Recent decreases (last 10-15 years) in net accumulation rates suggest a relationship with the decline in the use of tetraethyllead in gasoline.

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6. INORGANIC LEAD IN AQUATIC SEDIMENTS: GEOCHEMICAL PARTITIONING AND BIOAVAILABILITY

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Introduction*

Lead introduced into the aquatic environment, whether from atmospheric or terrestrial sources, tends to accumulate in sediments, where it is distributed among a variety of physico-chemical forms. As these different metal forms will generally exhibit different physical and chemical properties, measurement of the total lead concentration will provide little indication of the metal's potential interactions with abiotic or biotic components of the environment. The corollary, of course, is that knowledge of the speciation of lead will be useful for determining its origins and for understanding its geochemical behaviour (mobility/transport) and biological availability.

Metals in aquatic sediments may be:

- present in the interstitial water (fraction (o))
- adsorbed at particle surfaces (e.g. clays, humic acids; iron oxyhydroxides) (fraction (i))
- carbonate-bound (e.g. discrete carbonate minerals; co-precipitated with major carbonate phases) (fraction (ii))

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* This contribution is drawn in part from earlier publications: Campbell and Tessier, 1984, 1986; Tessier and Campbell, 1987.

- occluded in iron and/or manganese oxyhydroxides (e.g. discrete nodules; cement between particles; coatings on particles) (fraction (iii))
- organic-bound (e.g. bound up with organic matter, in either living or detrital form) (fraction (iv-a))
- sulphide-bound (e.g. amorphous sulphides, formed *in situ*; more crystalline forms) (fraction (iv-b))
- matrix-bound (e.g. bound in lattice positions in aluminosilicates, in resistant oxides or in resistant sulphides) (fraction (v).

The partitioning of lead among the non-detrital forms listed above (i.e. among fractions (i) - (iv)) will be affected by the physico-chemical conditions prevailing within the sediment. Important factors influencing partitioning will include: the nature and concentration of the solid phases present; the nature and concentration of the ligands present in the interstitial water; the nature and concentration of the other cations present in the interstitial water; the redox potential and pH; and the degree to which chemical equilibrium is attained (i.e. reaction kinetics). In contrast, metals bound in the residual fraction (v) will be relatively unaffected by these factors. In effect, the contribution of this 'detrital' fraction will largely be determined by the amount of clastic material present in the sediment.

In this contribution to the workshop, the literature pertaining to the partitioning of inorganic lead in sediments is summarized, and possible relationships between the partitioning of lead and its bioavailability to benthic organisms are discussed.

Lead Partioning in Sediments

Approaches

In principle, the partitioning of lead in aquatic sediments could be determined both by thermodynamic calculations (provided equilibrium conditions prevail) and by experimental techniques. Although the former approach holds considerable promise in this regard (Oakley et al., 1981; Luoma and Davis, 1983; Tessier et al., 1985), it is of limited application at the present time since the thermodynamic data needed for handling the complex sediment-interstitial water systems are as yet incomplete. Direct determination of specific lead-sediment associations is also difficult, if not impossible, because of the great variety of solid phases that can bind lead, the amorphous nature of these potential sinks and the relatively low lead concentrations involved. Thus, the only realistic means of studying lead partitioning in sediments at the present time is to fractionate the sediment physically and/or chemically.

Interstitial Water. Many techniques have been used for sampling sediment interstitial waters (fraction (o)): centrifugation of sediment samples and decantation; centrifugation, decantation and filtration; squeezing of sediment samples under moderate pressure; solvent displacement; and *in situ* dialysis (Carignan et al., 1985). For each of these methods extreme precautions must be taken to prevent analyte loss during sample handling (e.g. inadvertent introduction of oxygen, followed by co-precipitation of the metal of interest with iron/manganese oxyhydroxides), and to avoid possible contamination of the sample (e.g. by contact with inadequately cleaned samplers, filters, labware, etc., or by incomplete removal of particulate/colloidal material derived from the sediment matrix).

Particulate Material. Conceptually, the solid material can be partitioned into specific fractions (cf. (i) - (v) above); sequential extractions with appropriate reagents can then be devised to leach successive fractions 'selectively' from the sediment sample. Alternatively, the sediment may be fractionated physically, according to grain size or by density gradient separation, and the individual fractions analysed separately.

To extract sediment-bound metals 'selectively' from a particular form or phase, one may choose among a variety of different reagents (see Förstner, 1982, for a compilation of available extractants). These reagents fall naturally into classes of similar chemical behaviour, for example:

- concentrated inert electrolytes (desorption of electrostatically adsorbed metals)
- weak acids (dissolution of carbonate phases; desorption of specifically adsorbed metals)
- reducing agents (reduction of amorphous iron and/or manganese oxyhydroxides)
- complexing agents (competition for metals complexed with organic functional groups; dissolution of precipitates)
- oxidizing agents (oxidation of organic matter and sulphides)
- strong mineral acids (dissolution of resistant oxides, sulphides and aluminosilicates).

If the extractants are chosen in order of increasing strength, they can be used in sequential fashion; a representative example of this type of approach is shown in Figure 1 (Tessier et al., 1979).

Lead partitioning as determined by sequential extraction procedures will be influenced by such factors as the methods used to preserve the sediment

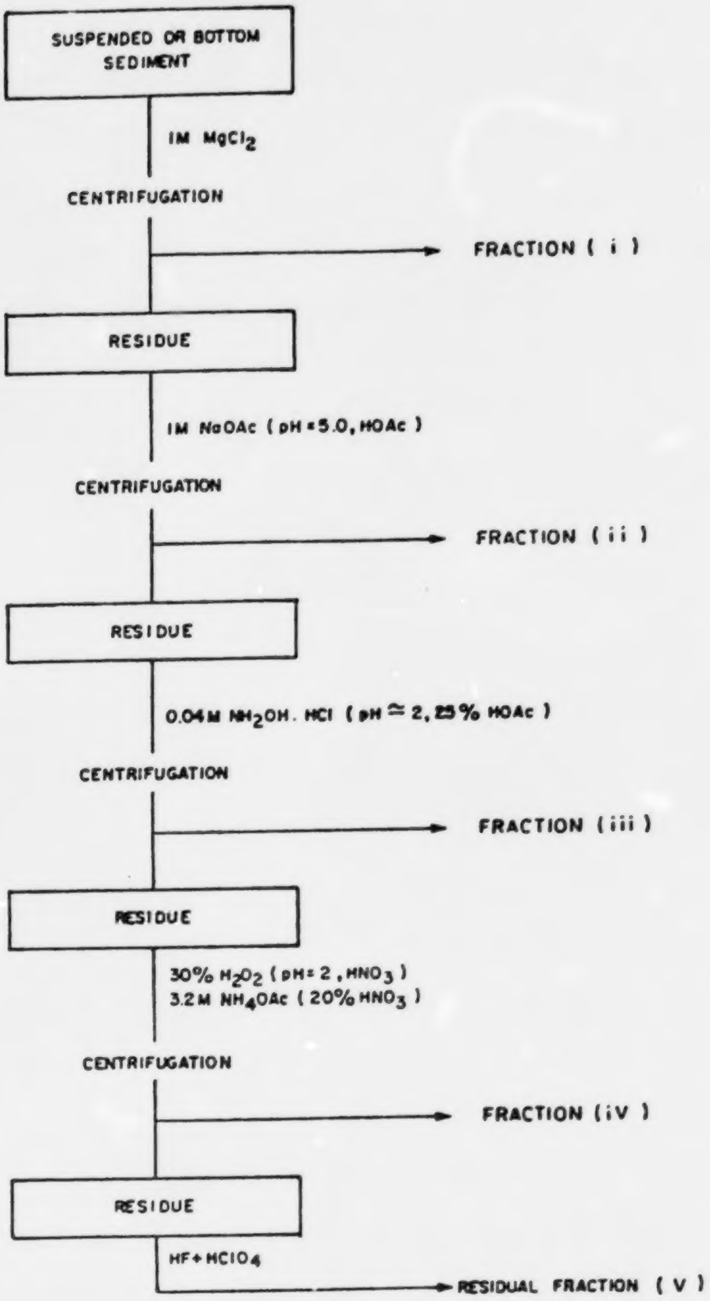

SUSPENDED OR BOTTOM SEDIMENT
1M $MgCl_2$
CENTRIFUGATION
FRACTION (i)
RESIDUE
1M NaOAc (pH = 5.0, HOAc)
CENTRIFUGATION
FRACTION (ii)
RESIDUE
0.04M $NH_2OH \cdot HCl$ (pH ≃ 2, 25% HOAc)
CENTRIFUGATION
FRACTION (iii)
RESIDUE
30% H_2O_2 (pH = 2, HNO_3)
3.2M NH_4OAc (20% HNO_3)
CENTRIFUGATION
FRACTION (iV)
RESIDUE
$HF + HClO_4$
RESIDUAL FRACTION (V)

Figure 1. Typical sequential extraction scheme for determining the partitioning of trace metals in aquatic sediments (Tessier et al., 1979).

sample (Rapin et al., 1986), the choice of reagents used for the various extraction steps, the extraction sequence, the contact time between the particulate material and the extractant, and the solid:extractant ratio (Tessier et al., 1979; Förstner, 1982, Robbins et al., 1984). In addition, the reagents available for the extraction of sediments are inherently unselective, and any sequential extraction procedure will unavoidably suffer from a certain lack of selectivity. It follows that the observed distribution of lead among various fractions will not necessarily reflect the relative contributions of discrete sediment phases, but rather should be considered as operationally defined by the methods of extraction.

Despite these limitations, tests to date (Tessier et al., 1979; Tessier et al., 1982a; Rapin and Förstner, 1983; Robbins et al., 1984) suggest that selectivity is reasonably satisfactory for low-sulphide (oxic) sediments. For sulphide-rich (anoxic) sediments, however, several lines of evidence indicate that the various extraction procedures currently in use are compromised by the tendency of metal-containing sulphide phases to be leached progressively rather than selectively from the host sediment (Rapin and Förstner, 1983; Rapin et al., 1986). Accordingly, we have limited our review to those studies reporting lead partitioning in properly preserved oxic surface sediments.

Results

Interstitial Water. Lead concentrations reported for sediment interstitial waters (IW) vary considerably (Table 1: 0.1-74 μg L^{-1}); the higher values must, however, be considered suspect. In studies of sediment cores, lead concentrations for successive strata often fluctuate wildly; most other metals show consistent trends and relatively smooth concentration profiles with depth. While some of this variation is no doubt real, related to geochemical

Table 1.

Lead concentrations in sediment interstitial waters.

Reference	Sediment Type (N)*	Sample Preparation**	$[Pb]_T$ ($\mu g\ g^{-1}$)	Speciation	Comments
Hart & Davies 1977	Creek (1) (surface)	C;F	59	labile (Chelex) 19% $[Pb]_T$; ultrafilterable (2 nm) 32% $[Pb]_T$	-
Matisoff et al. 1980	Lake (1) (core)	S	0.1-5	-	marked down-core fluctuation; $[S^{2-}]$ <10^{-7} M
Schierup & Larsen 1981	Lake (2) (core)	S	<1	-	-
Pedersen 1985	Coastal inlet (3)	C	0.06-3.5 (avg.~0.2)	-	down-core profiles "lack consistency"; variable contamination suspected
Carignan & Nriagu 1985	Lake (5)	D	<1 (two values 2-3 $\mu g\ L^{-1}$)	-	Sudbury region
Tessier et al. 1985	Lake (3)	D	2.5-6	-	Sudbury region
Duchart et al. 1973	Loch (4) (core)	S	<10-74	-	moderate down-core fluctuation; concentrations rather high...contamination?
Batley & Giles 1980	River (2) Estuary (1)	SD	0.2-0.6	labile (asv) 43-53% $[Pb]_T$	river > estuary
Abdullah & Reusch-Berg 1981	Fjord (1) (core)	S	0.5-2.9	labile (asv) 23-58% $[Pb]_T$, except in 0- 2.5-cm stratum (6%)	marked down-core fluctuation
Westerlund et al. 1984	Fjord (1) (core)	C;F	0.15	-	-
Rapin et al. 1983	Ocean (1) (core)	C	17-62	-	Baie de Villefranche, highly polluted; marked down-core fluctuation

* Sediment type: N = number of samples.
**Sample preparation: C = centrifugation; D = _in situ_ dialysis; F = filtration (0.45 μm); S = squeezing; SD = solvent displacement.

variability and differences in anthropogenic inputs, much may also reflect the more or less efficient exclusion of fine particulates and colloidal material from the sample (Carignan et al., 1985). Metal concentrations (μg g^{-1}) in this size fraction are often very high (Nissenbaum and Swaine, 1976; Elderfield, 1981). Comparison of the results obtained with different sampling techniques suggests that metal concentrations generally decrease in the sequence centrifugation > squeezing > _in situ_ dialysis, i.e. as removal of fine particulates and colloidal material becomes more efficient. Inadvertent contamination of the IW samples may also be a contributing factor (Patterson and Settle, 1976). Appropriate caution should thus be used in interpreting and comparing the compiled data.

In two cases lead speciation has been determined by electrochemical techniques (anodic stripping voltammetry (asv)) on sediment interstitial water, with somewhat different results: Batley and Giles (1980) reported that an appreciable proportion (43-53%, avg. 48%) of the lead from the IW displaced from their surface sediment samples was present in asv-labile form, whereas Abdullah and Reusch-Berg (1981) found that < 6% of the lead in their surface sediment sample (0- to 2.5-cm stratum) was in labile form. In lower strata, however, these latter authors noted somewhat higher proportions of labile lead (23-58%, avg. 42%).

Particulate Material. As defined by sequential extraction procedures, lead partitioning in sediments is strongly influenced by the techniques used for sediment preservation (Rapin et al., 1986). Accordingly, we have compiled only those results obtained with wet sediments (Table 2: 8 studies from the total of >30 that were identified). Total lead concentrations in these sediments range from 10 to >600 μg g^{-1}. With a single exception (Eisenreich et al., 1980), all the reported results were obtained with similar extraction procedures.

Several general trends can be discerned in Table 2. If the final fraction is ignored, i.e. if only the non-detrital lead is considered, the dominant fraction is invariably that associated with the reducible iron/manganese oxides. Similarly, the contribution of the exchangeable fraction extracted with a concentrated inert electrolyte is generally quantitatively negligible; the results reported by White (1984) for Darts Lake (Adirondack Mountains, NY) constitute the only exception to this statement. Moderate and variable contributions to the total lead burden are afforded by the remaining non-detrital fractions, i.e. those extracted with weak acids or with an oxidizing reagent. As might be anticipated on the basis of differing proportions of clastic material in the sediment samples, the relative importance of the silicate and resistant mineral fraction is rather variable (Table 2). This fraction is generally more important in fluvial sediments (Wilber and Hunter, 1979; Eisenreich et al., 1980; Tessier et al., 1982a) than for lacustrine samples.

The importance of iron/manganese oxides in controlling lead partitioning in sediments is also borne out by statistical analysis of analytical data from a variety of sedimentary environments. In a particularly thorough example of this approach, Luoma and Bryan (1981) considered analytical results for 19 estuaries (50 samples of surficial oxidized sediment; 10 different extraction techniques); correlations were sought between various extractable metals (including lead) and possible geochemical sinks (iron oxides; manganese oxides; humic acids). The initial correlations were checked on subsets of the original population, chosen to accentuate certain sediment properties (e.g. low (Fe), high (Mn), low (humic acids)). Statistical analysis within such

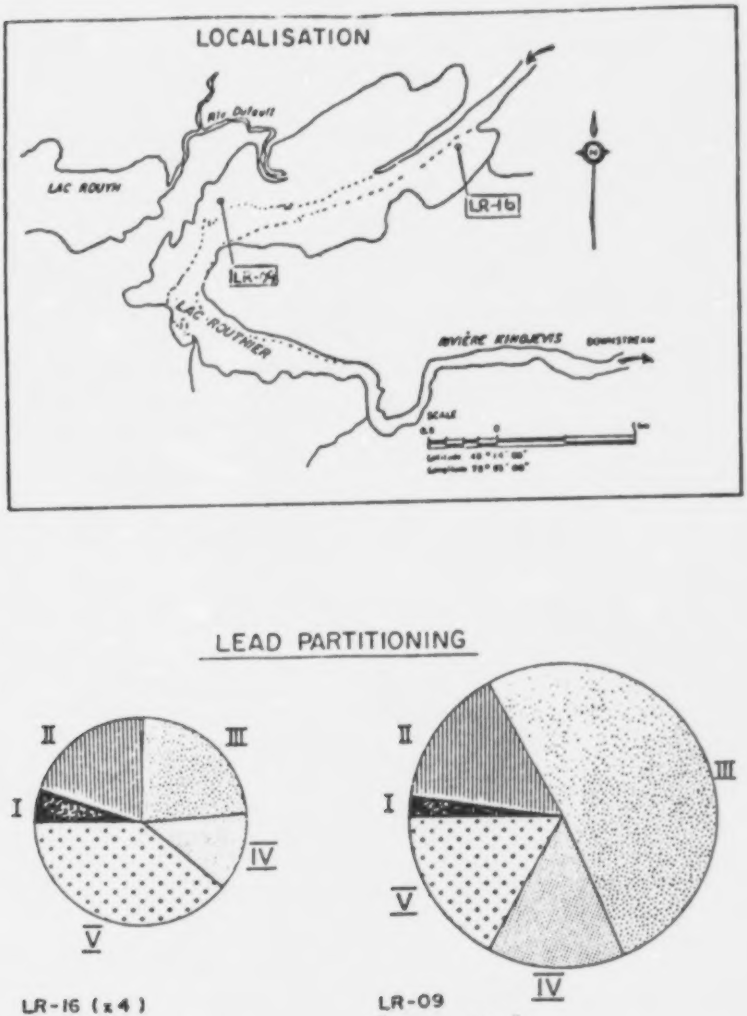
Table 2.

Lead partitioning in sediments.

Reference	Sediment Type (N)	Preservation	$[Pb]_T$ ($\mu g\ g^{-1}$)	Extraction Procedure	Results/Comments
Wilber & Hunter 1979	River (3)	Fresh	14-71	1. NH_4OAc 3. NH_2OH/HNO_3 4. $H_2O_2/HNO_3//NH_4OAc$ 5. HNO_3/HCl	F5 > F3 ~ F4 > F1
Eisenreich et al. 1980	River (5) (suspended solids)	Fresh	?	1. $MgCl_2$ 2. $Na_2P_2O_7$ 3. HCl 4. $HNO_3/HCl/HF$	F2 > F4 > F3 >> F1
Tessier et al. 1982(a)	River (5) (surface)	Frozen; thawed	10-612	1. $MgCl_2$ 2. $NaOAc/HOAc$ 3. $NH_2OH/HOAc$ 4. $H_2O_2/HNO_3//NH_4OAc$ 5. $HF/HClO_4$	F5 ~ F3 >> F4 > F2 > F1 ~ 0
Tessier et al. 1984	Lake (8) (surface)	4°C; wet (< 70 µm)	30-150	1. $MgCl_2$ 2. $NaOAc/HOAc$ 3. $NH_2OH/HOAc$ 4. $H_2O_2/HNO_3//NH_4OAc$ 5. $HF/HClO_4$	F3 > F5 >> F2 ~ F4 > F1 ~ 0
Tessier et al. 1985	Lake (3) (surface)	4°C; wet	16-189	1. $MgCl_2$ 2. $NaOAc/HOAc$ 3a. NH_2OH/HNO_3 (20°C) 3b. $NH_2OH/HOAc$ (96°C) 4. $H_2O_2/HNO_3//NH_4OAc$ 5. $HF/HClO_4$	F3b > F3a > F2 > F4 ~ F5 > F1
White 1984	Lake (1) (core)	4°C; wet	90-320	1. $MgCl_2$ 3. $NH_2OH/HOAc$ 4. $H_2O_2/HNO_3//NH_4OAc$ 5. HNO_3	F3 >> F1 > F4 ~ F5
Lion et al. 1982	Estuary (1) (surface)	4°C; wet	50	1. $MgCl_2$ 2. $NaOAc/HOAc$ 3. $NH_2OH/HOAc$ 4. $H_2O_2/HNO_3//NH_4OAc$	F3 >> F4 > F2 > F1 ~ 0

subsets indicated that trace metals were partitioned among several substrates in most sediments, that the substrates competed with one another for the metals and that the outcome of the competition was strongly influenced by the concentrations of the different substrates in the sediment. Concentrations of extractable lead in sediments correlated weakly, but significantly, with sediment-bound iron and manganese among all samples. A very strong correlation of lead with HCl-extractable iron (but not total iron) was observed among stations where either manganese or organic carbon was low in concentration. Similarly, a strong correlation of lead with manganese was observed among stations where the (Fe)/(Mn) ratio was low, suggesting effective competition between extractable iron and manganese for the binding of lead in sediments (Luoma and Bryan, 1981).

The role of iron/manganese hydrous oxides as a sink for anthropogenic lead is further illustrated in Figure 2, which shows lead partitioning in the sediments at two stations in Lac Routhier, a small lake in north-western Quebec. Station LR-09 is located downstream from the confluence of the Dufault river, which in the past was heavily contaminated by the mining and smelting activities in nearby Rouyn-Noranda and constituted a point source of lead pollution; station LR-16 is situated immediately upstream from this input and can be considered as a control site. Anthropogenic inputs of lead would be expected to increase the total lead concentration in the sediments and, as lead of such origin is unlikely to be bound in lattice positions in resistant minerals, the relative contribution of the residual fraction to the total particulate lead concentration should decrease. With reference to Figure 2, these effects would correspond to an increase in the circle area, a decrease in the sector representing the residual fraction and an increase in the con-



LR-16 (x4) [8.5 mg/kg] (%)	FRACTION	LR-09 [283 mg/kg] (%)
5	I	3
20	II	15
24	III	51
12	IV	15
39	V	17

Figure 2. Influence of anthropogenic inputs on lead partitioning in lake sediments (Lac Routhier, Québec: Tessier et al., 1982b). Stations LR-16 and LR-09 are located upstream and downstream, respectively, with respect to the pollution sources, Rivière Dufault (see inset).

tribution of one or more of the non-residual fractions (Tessier et al., 1980); comparison of the results for stations LR-16 and LR-09 reveals such a trend. At the contaminated site (station LR-09), the total lead concentration has increased from 9 to 283 mg kg^{-1}, the relative contribution of the residual fraction has diminished (from 39 to 17%) and the proportion of lead associated with the reducible iron/manganese oxides has increased (from 24 to 51%).

This sensitivity of fraction (iii) to anthropogenic inputs of lead is consistent with the known scavenging efficiency of iron/manganese oxides for this metal, as demonstrated in the laboratory with various synthetic hydrous oxides (Kinniburgh and Jackson, 1981; Balistrieri and Murray, 1982). Although complex and not fully understood, the scavenging action of these oxides in the environment is generally thought to be the result of two complementary processes: adsorption and co-precipitation (Jenne, 1968; Hem, 1976, 1977). In rivers and lakes, these geochemical phases may result from physical erosion of soil particles already containing iron/manganese oxides, from *in situ* oxidation of allochthonous inputs of dissolved iron and manganese (e.g. ground water containing Mn(II) and Fe(II), or acid mine waters) or from sediment diagenesis (vertical diffusion of Mn(II) and Fe(II) from reduced sediments upward towards the sediment-water interface, followed by oxidation).

Influence of Acidification. The adsorption of metals (including lead) onto various solid substrates is inherently sensitive to pH changes. Interactions of lead with sediments, or with individual sediment components (e.g. clays; iron or manganese oxides; humic acids), have been studied in the laboratory under different pH conditions, usually in stirred suspensions. If the percentage of metal adsorbed is plotted as a function of pH, a sigmoidal relation is usually obtained, with an abrupt increase in the amount of adsorbed metal occurring over a narrow pH range as the pH is raised (the so-called 'adsorption edge'; Figure 3). In such a plot the pH at which 50% of the original cation concentration is adsorbed, pH_{50}, is a useful parameter for comparing the adsorption of a particular metal (lead) on different solid phases (Kinniburgh and Jackson, 1981); see Table 3 for an example with two different solid phases, $Fe(OH)_3$ gel and $Al(OH)_3$ gel.

These laboratory studies are useful in that they illustrate the potential effects on lead mobility of a relatively small change in pH, and demonstrate the selectivity of certain phases for different metal cations; with hydrous metal oxides, lead is clearly one of the most tightly bound of the tested cations, and very low pH values are needed to promote its desorption. Note, however, that in a given metal-solid system the position and shape of the pH adsorption 'edge', and thus the value of pH_{50}, will depend on such factors as the concentration of the solid phase, its surface characteristics, the initial concentration of the adsorbing metal and the nature and concentration of any dissolved ligands present (Davis and Leckie, 1978; Benjamin and Leckie, 1981a, b). Note, too, that relatively few studies have been performed with natural sediments (Table 4), and virtually none have been carried out at the high solid/solution ratios that prevail in a natural sediment. Accordingly, the quantitative transposition of the results of this type of laboratory study to field conditions is not yet feasible.

Recent field data obtained by our research group (Tessier et al., 1985) do, however, provide qualitative support for the trends described above. Concentrations of cadmium, copper, nickel, lead and zinc were measured in sediment pore waters in lakes of different pH located on the Canadian Precambrian Shield (by in situ dialysis); metal partitioning in the adjacent surficial

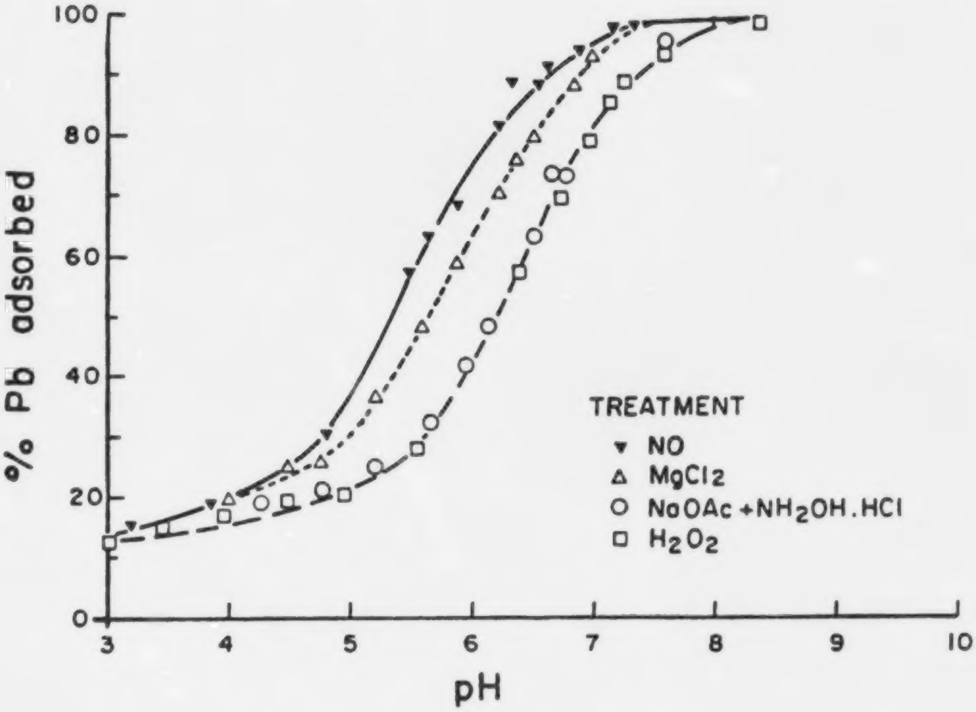


Figure 3. pH adsorption curves for Pb on natural sediments (San Francisco Bay estuary: Lion et al., 1982). The adsorption curves were determined on fresh, untreated sediments (▼), as well as on sediments that had been pretreated according to the extraction scheme shown in Figure 1 (△, ○, □). Note the pronounced effect attributable to the removal of the reducible Fe/Mn oxides.

Table 3.

Adsorption of trace metals on colloidal metal hydroxides (from Kinniburgh and Jackson, 1981).

$Fe(OH)_3$ gel*

Metal**:	Pb	Cu	Zn	Ni	Cd ~ Co
pH_{50}***:	3.0	4.3	5.3	5.7	5.9

$Al(OH)_3$ gel

Metal :	Cu	Pb	Zn	Ni	Cd ~ Co
pH_{50} :	4.8	5.2	5.6	6.3	6.6

* Gel concentration: 9.3×10^{-2} M Al or Fe.
** Trace metal concentration: 1.25×10^{-4} M.
***pH_{50}: pH at which 50% of added metal concentration is adsorbed.

Table 4.

Values of pH_{50} for the adsorption of lead on natural sediments.

Sampling Site	[Pb]* (μM)	[Sediment] ($g\ L^{-1}$)	pH_{50}	Reference
Four rivers, New South Wales, Australia	9.7	50	2.2-2.4	Rendell et al., 1980
Anonymous river, UK	1	1.1	~ 4	Salim and Cooksey, 1980
San Francisco Bay estuary, USA	10	1.0	4.5	Lion et al., 1982
	0.1	0.25	3.8	
	1	0.25	4.6	Lion et al., 1982
	10	0.25	5.6	

* [Pb]: added lead concentration.

sediments was determined by a sequential extraction procedure similar to that shown in Figure 1. Apparent overall equilibrium constants were then calculated for the adsorption of each metal onto the natural iron oxyhydroxides and compared with equilibrium constants obtained for adsorption onto synthetic iron oxyhydroxides in the laboratory. The binding strength sequence observed for the field data agreed with that observed for the synthetic iron oxyhydroxides: Pb > Cu > Zn > Cd, Ni. In addition, for the last three metals the influence of pH was consistent with the laboratory data (i.e. desorption at low pH, with resulting higher concentrations in the pore water). For copper and lead, however, adsorption proved relatively insensitive to pH changes and remained high even at an *in situ* pH of 4.6. The resulting levels of lead in the sediment pore water were even lower than would have been predicted from the laboratory experiments with synthetic oxides in ligand-free systems. A possible explanation of this enhanced adsorption at low pH would be the formation of ternary complexes involving lead, the iron oxyhydroxide surface and dissolved organic ligands present in the pore water (Tessier et al., 1985).

Thus, both laboratory and field data indicate that anthropogenic lead present in lake sediments is likely to be relatively insensitive to environmental acidification in the pH range 7-4 (Campbell et al., 1985).

Lead Bioavailability in Sediments

General Principles

As has been mentioned elsewhere during this workshop (Norton and Kahl, p. 97), lead of anthropogenic origin tends to accumulate in lacustrine sediments. Lead concentrations at the sediment-water interface are often 10^3-10^4 times those in the overlying water. Clearly such concentrations pose a potential danger for benthic organisms living at the sediment-water interface, both those that ingest sediments (Type B) and those that simply live in close association with the sediments (Type A). Given the inherent toxicity of lead (Kaiser, 1980) and the disproportionately important role played by benthic organisms in overall lake metabolism (Schindler, 1985), the estimation of the bioavailability of lead in sediments assumes considerable importance.

Benthic organisms can take up metals directly from the sediment interstitial water* and/or from particulate material. Thus the uptake pathway(s) used by a given organism will dictate the geochemical approach to estimating lead bioavailability (Figure 4). For Type A organisms that live in intimate contact with the sediments but are incapable of ingesting particulate material (e.g. benthic algae; rooted aquatic plants), the obvious geochemical phase to consider is the interstitial water itself. An alternative to the direct measurement of interstitial water characteristics might be to determine metal concentrations in those sediment forms that are in equilibrium with interstitial water:

$$\equiv S(1)\text{-}Pb \xrightleftharpoons{K} Pb^{2+}{}_{i} + \equiv S(1) \qquad (1)$$

$$\equiv S(2)\text{-}Pb \xrightleftharpoons{K} Pb^{2+}{}_{i} + \equiv S(2) \qquad (2)$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$\equiv S(n)\text{-}Pb \xrightleftharpoons{K_n} Pb^{2+}{}_{i} + \equiv S(n) \qquad (3)$$

---

* The definition of 'interstitial' water will differ among benthic species and may include, in different cases: anoxic waters for organisms in contact with deeper sediments; oxic waters near the surface for organisms living within the sediment, but whose primary environmental contact is above the redox interface; or waters at the sediment-water interface for suspension-feeders.

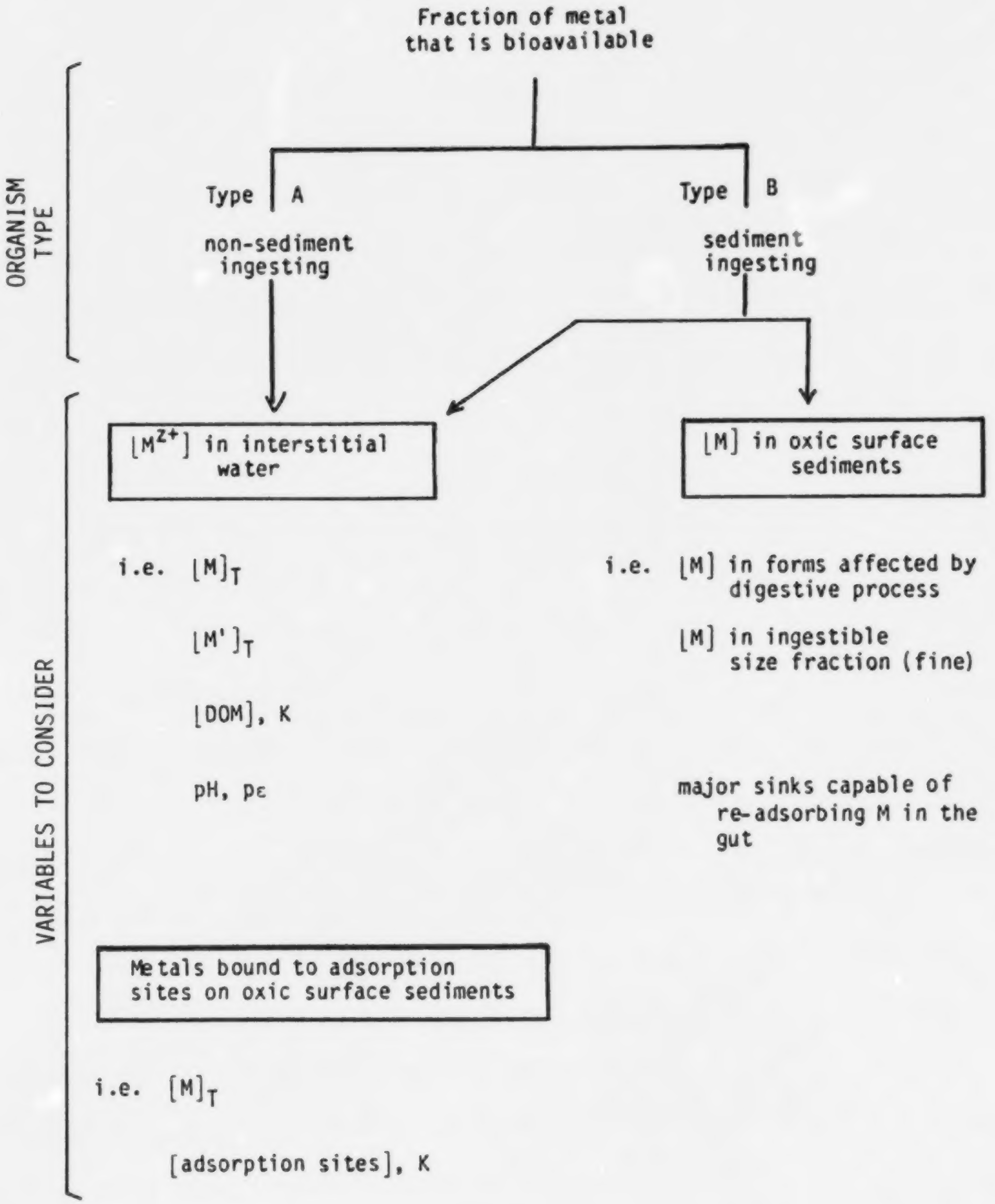

Fraction of metal that is bioavailable
ORGANISM TYPE
Type A
non-sediment ingesting
Type B
sediment ingesting
VARIABLES TO CONSIDER
[M^{z+}] in interstitial water
i.e. [M]_T
[M']_T
[DOM], K
pH, pε
[M] in oxic surface sediments
i.e. [M] in forms affected by digestive process
[M] in ingestible size fraction (fine)
major sinks capable of re-adsorbing M in the gut
Metals bound to adsorption sites on oxic surface sediments
i.e. [M]_T
[adsorption sites], K

Figure 4. Geochemical evaluation of the bioavailability of trace metals in sediments - general considerations (NRCC, 1986). Definition of terms: M = metal of concern; M^1 = competing metal; M^{2+} = free aquo ion; [ ] = concentration; $[\ ]_T$ = total concentration; DOM = dissolved organic matter; pε = redox potential; K = thermodynamic stability constant.

$$[\mathrm{Pb}^{2+}]_i = \frac{\{\equiv S(1)\text{-Pb}\}}{\{\equiv S(1)\}\cdot K_1} = \frac{\{\equiv S(2)\text{-Pb}\}}{\{\equiv S(2)\}\cdot K_2} = \cdots = \frac{\{\equiv S(n)\text{-Pb}\}}{\{\equiv S(n)\}\cdot K_n} \qquad (4)$$

where $[\mathrm{Pb}^{2+}]_i$ is the free metal ion present in the interstitial water; $\equiv S(1)$, $\equiv S(2)$, ...$\equiv S(n)$ are all solid substrates capable of binding lead (e.g. hydrous oxides of Fe, Mn, Al, Si; clays; humic substances); $\equiv S(n)$-Pb is lead bound to substrate $\equiv S(n)$; and K_1, K_2 ... K_n are the conditional equilibrium constants for the respective reactions. In such cases, the relevant parameter will not be the total metal concentration in the particulate material, but rather that proportion of the metal in adsorptive equilibrium with the solid surfaces ($\equiv S(1)$-Pb, $\equiv S(2)$-Pb, etc.), together with the concentration of the solid phase(s), $\{\equiv S(n)\}$, responsible for binding the metal in this form. **In this approach, the ratio ($\{\equiv S(n)\text{-Pb}\}/\ \{S(n)\}$) would represent a surrogate measure of $[\mathrm{Pb}^{2+}]_i$ (see Eq. (4)), and thus could be a useful predictor of lead bioaccumulation.** Note that the concentration of adsorbed or 'exchangeable' metal is not normally in itself sufficient to estimate $[\mathrm{Pb}^{2+}]_i$ or to estimate lead bioavailability. In effect, high levels of adsorbed metal in a given sediment may simply reflect an abundance of adsorbing surfaces, rather than a high value of $[\mathrm{Pb}^{2+}]_i$ in the interstitial water.

The reasoning described to this point for Type A organisms also applies to Type B organisms (Figure 4), i.e. those capable of ingesting sediments and taking up lead from the particulate phases. To these considerations, however, must be added an evaluation of the possible uptake of lead during digestion of the sediments in the gut. Since even in the gut metals must normally pass into solution before they can be assimilated, the obvious geochemical phases to consider are those which are affected by passage through the digestive tract. Digestive chemistry thus assumes considerable importance; to evaluate bioavailability it seems logical to simulate or at least approach the conditions prevailing in the gut, using a chemical extraction technique. The residence time of the sediments in the target organism is also of importance, since the desorption and/or dissolution reactions involved in the digestive process may be slow. In addition, particle size must be considered, since Type B organisms may be selective in their feeding/ingestion habits and digestive extraction will be more efficient as particle size decreases.

With both Type A and Type B organisms, lead uptake from solution may be influenced by metal-metal interactions, for example competition between lead and other dissolved metals for a given uptake site on a cell membrane:

$$\begin{tikzcd}
\mathrm{Pb}\ + & & \mathrm{Pb} - \text{L-membrane} \arrow[dl, shift left] \arrow[rr, "\text{transport of Pb}"] & & \cdots \\
& \text{L-membrane} \arrow[ur, shift left] \arrow[dr, shift left] & & & \\
M^1\ + & & M^1 - \text{L-membrane} \arrow[ul, shift left] & &
\end{tikzcd}$$

where M^1 = competing metal, and L-membrane = metal transport site on the cell membrane. For Type B organisms, knowledge of the concentration of other metals solubilized during the digestive process might thus be used to improve the prediction of the bioavailability of lead. Alternatively, competition may occur for solubilized lead, between the uptake sites on the one hand and the undigested sediment on the other (i.e. those solid phases least affected by the digestive process, including clays; iron-oxyhydroxides; manganese-oxyhydroxides; humic substances):

$$\mathrm{Pb}\quad \begin{array}{l} \text{L-membrane} \rightleftharpoons \text{Pb - L-membrane} \xrightarrow{\text{transport of Pb}} \cdots \\ (-0)_n\text{- substrate} \rightleftharpoons \text{Pb -}(0)_n\text{- substrate} \end{array}$$

where $(-0)_n$- substrate = a potential adsorption site on the undigested sediment. If such competition does occur, the bioavailability of lead will be lower in sediments rich in one or more of these 'ameliorative' phases.

Results

Aquatic Macrophytes. Two pathways exist for the accumulation of lead in the stems and leaves of freshwater macrophytes: (i) direct uptake from the water column, and (ii) uptake from the interstitial water in the sediments, followed by acropetal translocation from the roots to the stems and leaves. This same duality of pathways exists for other solutes (e.g. phosphorus), and both accumulation routes may be operative in the same plant (Denny, 1980). For submerged rooted species in a field situation, it will clearly be difficult to distinguish between the two possible uptake vectors; in such cases the least ambiguous 'integrator' of metal bioavailability in the sediments will be the underground parts of the plant including the roots and rhizome (Chiaudani, 1969; Welsh and Denny, 1980; Schierup and Larsen, 1981). For emergent species, the metal content of the above-ground parts of the plant constitutes an indicator of the bioavailability of the metal of concern in the host sediment, provided any contribution of airborne particulates to plant leaf surfaces can be discounted (Lee et al., 1978), and uptake via the submerged portion of the item is negligible.

Literature concerning the prediction of lead accumulation by aquatic macrophytes is scarce. If uptake from sediment interstitial water were widespread, one might expect the concentration of 'available' lead in the sediment substrate to be related to the metal concentration in the plant. However, a literature review of some 18 cases where metal concentrations had been determined both in freshwater plants and in the underlying sediments (Table 5) revealed that ≈ 40% of the cases showed no relationships between these two parameters; in an additional 2 cases, a negative relation was observed between the metal content of the plant, $\{Pb\}_p$, and that of the sediments, $\{Pb\}_{sed}$. A possible explanation for this apparent independence of $\{Pb\}_{sed}$ and $\{Pb\}_p$, besides the obvious one that metal uptake directly from the water column masks sediment-plant relationships, is that workers in this area have largely ignored the partitioning of the lead associated with the sediments, and have sought correlations between $\{Pb\}_p$ and the total lead concentration in the sediment rather than with a 'bioavailable' fraction. As discussed earlier, one might anticipate an improved prediction of metal accumulation by aquatic plants if metal partitioning in the host sediment were considered.

Freshwater macrophytes. Only one study was found where attempts had been made to predict lead concentrations in freshwater plants from lead partitioning data in the adjacent sediments (Table 6: case #1). But this example was not a true field study. Highly contaminated sediments were collected, returned to the laboratory and used as the substrate for growing Cyperus esculentus, a freshwater marsh plant, under controlled conditions simulating either reduced ('flooded') or oxidized ('upland') situations (Folsom and Lee, 1981; Lee et al., 1983). Sediment extractions were performed with DTPA (diethylenetriaminepentaacetate), an organic chelator commonly used to estimate the concentration of 'bioavailable' nutrients and metals in soils (Lindsay and Norvell, 1978). For the simulated flooded conditions, extractable lead proved a better predictor of plant lead content than did the total

Table 5.

Bioavailability of sediment-bound Pb to rooted aquatic plants (freshwater).

Species	Plant Part	Relation to sediment [Pb]	Number of sites	Reference
Submerged:				
Nymphaea odorata	leaves leaves + stems	+ve 0	2 5	Mudroch & Capobianco 1978
Potamogeton crispus	stems	+ve	5	Welsh & Denny 1980
Potamogeton perfoliatus	stems	+ve	5	Welsh & Denny 1980
	whole plant	0	11	Gommes & Muntau 1981
Elodea canadensis	leaves + stems	+ve	10	Welsh & Denny 1980
		+ve	2	Mayes et al. 1977
Myriophyllum alterniflorum	stems	+ve	9	Welsh & Denny 1980
Myriophyllum exalbescens	leaves	0	6	Franzin & McFarlane 1980
Myriophyllum spicatum	whole plant	0	30	Gommes & Muntau 1981
Myriophyllum heterophyllum	whole plant	-ve	2	Mudroch & Capobianco 1978
Glyceria fluitans	leaves + stems	+ve	10	Harding & Whitton 1978
Eriocaulon septangulare	whole plant	0	66	Miller et al. 1983
Lagarosiphon major	whole plant	+ve	22	Gommes & Muntau 1981
Emergent:				
Typha latifolia	roots	+ve	2	Mudroch & Capobianco 1978
Lythrum salicaria	leaves + stems	0	2	Mudroch & Capobianco 1978
Phragmites australis	leaves, stems, rhizomes	-ve	2	Schierup & Larsen 1981
Spartina alterniflora	whole plant	0	6	Dunstan et al. 1975

Table 6.

Examples of the use of sediment extraction techniques to predict the bioavailability of sediment-bound Pb to rooted macrophytes.

Species	Plant part	Metal	N*	Study type**	Sediment extraction procedure	Prediction of plant metal accumulation (coefficient of determination)***	Reference
Emergent plants (freshwater):							
1. *Cyperus esculentus* (chufa)	above-ground	Pb	14	L	DTPA (0.005M)/pH 7.3	'upland' conditions: NS	Folsom & Lee 1981 Lee et al. 1982, 1983
		Pb	14	L		'flooded' conditions: Pb extracted with DTPA ($r^2 = 0.26$)	
Submerged plants (estuarine):							
2. *Spartina alterniflora* (cord grass)	above-ground (leaf)	Pb	79	F	H_2O	NS	Lee et al. 1978
					NH_4OAc (1M)/pH ambient		
					DTPA (0.005M)/pH 7.3		
					HCl (0.05M), H_2SO_4 (0.013M) (fresh sediment; non-sequential extraction)		
3. *Spartina patens* (cord grass)	above-ground (leaf)	Pb	23	F	(as in #2)	Pb extracted with HCl/H_2SO_4 ($r^2 = 0.40$) with NH_4OAc ($r^2 = 0.17$)	Lee et al. 1978
4. *Distichlis spicata* (spike grass)	above-ground (leaf)	Pb	25	F	(as in #2)	Pb extracted with DTPA ($r^2 = 0.25$)	Lee et al. 1978

* N = number of sites.

** Study type: F = field survey; L = laboratory study.

***NS = no significant correlations between $[Pb]_p$ and extractable Pb.

lead concentration in the sediment. For 'upland' situations, however, neither DTPA-extractable nor total lead was related to lead bioaccumulation.

Estuarine/coastal macrophytes. For rooted marine plants, a single field study was identified where attempts had been made to refine estimates of lead bioavailability by sediment extraction techniques (Lee et al., 1978). Four extractants (distilled H_2O; NH_4OAc; DTPA; HCl/H_2SO_4) were tested and the concentrations of extracted metal were used to predict lead uptake by salt marsh plants at existing dredged material disposal sites. Of these, the dilute acid extraction (HCl/H_2SO_4) showed good potential for predicting lead accumulation in one of the three species studied, Spartina patens (Table 6: case #3). On the other hand, DTPA-extractable lead proved to be the best predictor of lead accumulation in Distichlis spicata (case #4). For the third species, Spartina alterniflora, none of the extractants provided a reliable estimate of bioavailable lead.

Benthic Invertebrates. Deposit-feeding invertebrates are directly exposed to sediment-bound metals, and are capable of accumulating metals from interstitial waters and/or from ingested sediment. Controlled laboratory feeding experiments, often involving the use of artificial sediments, have shown that uptake of a given metal may differ markedly among different sediment types (e.g. iron oxides, manganese oxides, organic materials, carbonates; Luoma and Jenne, 1977). The ranking of these different solid phases, as a function of the 'bioavailability' of their associated metals, may vary from one metal to another (Luoma, 1983). On the basis of such results, and in accord with the earlier discussion, one might anticipate the existence of consistent relationships between lead accumulation in benthic invertebrates and lead partitioning in the adjacent or host sediment. Indeed, attempts to relate lead concentrations in various benthic species to those in the adjacent sediment are more numerous (and more successful) than for the aquatic macrophytes discussed earlier.

In the following section we consider results from field surveys in which surficial sediment samples and benthic invertebrates were collected along gradients of sediment lead concentration, and where attempts were made to predict lead accumulation in the organisms from the lead content of the host sediment. Since simple relationships between $\{Pb\}_{organism}$ and the total lead concentration in the sediment are seldom found in such studies (e.g. Neff et al., 1978; Marquenie et al., 1983; Bryan, 1985), the present compilation has been limited to those investigations for which lead partitioning data are reported for the sediments.

Freshwater invertebrates. For freshwater systems three field surveys were identified which satisfied the criteria outlined above (Table 7). Extractants used to evaluate metal partitioning included concentrated electrolytes ($MgCl_2$; NH_4OAc), weak and strong acids (HOAc; HCl), a reducing agent designed to solubilize amorphous iron and manganese oxyhydroxides ($NH_2OH \cdot HCl$) and an acidic oxidizing solution (H_2O_2, HNO_3).

In filter-feeding molluscs, Elliptio complanata and Anodonta grandis, lead levels in gills were best related not to the total lead concentrations in the adjacent sediment, but rather to one or more of the relatively easily extracted fractions present in the fine sediments (<70 μm, the ingestible size fraction). Accumulation of lead was also influenced by the protective or competitive effect of certain other sediment constituents, notably the amorphous iron oxyhydroxides. The best predictions of lead levels in the molluscs were obtained when lead concentrations extracted from the sediments were normalized

Table 7.

Examples of the use of sediment extraction techniques to predict the bioavailability of sediment-bound Pb to freshwater benthic invertebrates.

Species	Organism part	Metal	N*	Study type**	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)	Reference
Filter-feeders:							
1. Elliptio complanata (mollusc)	gills	Pb	8	F	- $MgCl_2$ (0.5M)/pH 7 - NaOAc (1M), HOAc/pH 5 - $NH_2OH \cdot HCl$ (0.04M), HOAc (25%) / 95°C - H_2O_2 (30%), HNC_3/85°C pH 2 - HF, $HClO_4$ (5:1)/digestion (fresh sediment, < 70 µm; sequential)	Pb extracted in fractions 1→3 ÷ Fe extracted with $NH_2OH \cdot HCl$ ($r^2 = 0.93$)	Tessier et al. 1984
2. Anodonta grandis (mollusc)	gills	Pb	6	F	(as in # 1)	[Pb/Fe] extracted with $NH_2OH \cdot HCl$ ($r^2 = 0.76$)	Tessier et al 1982b
3. Oligochaetes (unidentified; mainly Limnodrilus hoffmeisteri and Tubifex tubifex)	whole	Pb	12	F	- centrifugation - NH_4OAc (1.3M)/pH 7 - $NH_2OH \cdot HCl$ (0.1M), HNO_3/pH 2 - H_2O_2 (30%), HNO_3/95°C pH 2 - HCl (3M)/80°C - HF (70%), HNO_3/digestion (fresh sediment, < 2 mm; sequential)	total Pb ($r^2 = 0.46$, linear); Pb_2 extracted with $NH_2OH \cdot HCl$ ($r^2 = 0.35$)	Bindra & Hall 1977 Hall & Bindra 1979

* N = number of sites.
**Study type: F = field survey.

with respect to the amorphous iron concentration.

Results for deposit-feeding oligochaetes differed from those for the molluscs in that total lead in the sediments was the best predictor for lead levels in the organisms. However, no attempts were made by the authors (Bindra and Hall, 1977; Hall and Bindra, 1979) to improve the predictions by normalizing lead concentrations in the sediment with respect to other sediment constituents.

Estuarine/coastal invertebrates. Studies relating lead bioaccumulation by macroinvertebrates to lead levels in sediments are more numerous for the estuarine environment than for freshwater systems. Many extractants have been explored (Table 8); the individual reagents have usually been applied in non-sequential fashion to the fine sediment fraction (<100 µm or <250 µm). Three invertebrate species have been studied extensively: two deposit-feeding clams occupying similar ecological niches (Scrobicularia plana; Macoma balthica), and a polychaete (Nereis diversicolor). Lead accumulation in these organisms was best predicted from metal concentrations in one or more of the more readily extracted fractions present in the sediments. Normalization of these sediment metal concentrations with respect to the concentrations of one of the major metal sinks present in the sediment, either amorphous iron oxyhydroxides or organic matter, frequently led to marked improvements in the predictions of metal accumulation (Table 8).

Summary

In this contribution to the workshop on pathways, cycling and transformation of lead in the environment, we have considered the geochemical fate of inorganic lead of anthropogenic origin in aquatic sediments, and have examined relationships between lead partitioning in sediments and its bioavailability to benthic organisms. The following points should be emphasized:

1) Geochemical partitioning

- lead concentrations reported for sediment interstitial water vary considerably (Table 1 : 0.1-74 μg L^{-1}); the high values are considered suspect
- lead of anthropogenic origin tends to accumulate in aquatic sediments, where the dominant geochemical fraction is consistently that associated with reducible iron/manganese oxides (Table 2)
- both laboratory and field data indicate that anthropogenic lead present in lake sediments is likely to be relatively insensitive to environmental acidification.

2) Bioavailability

- information regarding the prediction of lead accumulation by aquatic macrophytes from sediments is scarce; for benthic invertebrates the knowledge base is somewhat better, at least for estuarine species
- for macrophytes, results published to date suggest that marked species-to-species differences may exist (cf. Table 6: DTPA-extractable lead was a reasonable predictor of lead accumulation by Distichlis spicata, but not by Spartina alterniflora or S. patens)
- although such sediment characteristics as pH, redox potential, organic matter content and amorphous iron concentration have been shown qualitatively to influence metal accumulation by aquatic macrophytes, few attempts have been made to incorporate these variables into predictive equations applicable in a field setting; this would

Table 8.

Examples of the use of sediment extraction techniques to predict the bioavailability of sediment-bound Pb to marine benthic invertebrates.

Species	Organism part	Metal	N*	Study type**	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)	Reference
Deposit-feeders:							
1. Scrobicularia plana (mollusc)	whole	Pb	37	F	- NH_4OAc (1M) - $(NH_4)_2C_2O_4$ (0.2M), $H_2C_2O_4$ - HOAc (25%); HNO_3/pH 2.2 - $NH_2OH{\cdot}HCl$ (0.1M), HNO_3 (0.01M) (fresh sediment, < 100 µm; non-sequential) - HCl (1M) - HNO_3 (15M)/digestion (dried sediment, non-sequential)	(Pb/Fe) extracted with HCl (r^2 = 0.98, linear; 0.88, log-log)	Luoma & Bryan 1978
2. Macoma balthica (mollusc)	whole	Pb	15	F	- HCl (1M) (fresh sediment, < 100 µm)	(Pb/Fe) extracted with HCl (r^2 = 0.58, log-log)	Bryan 1985
3. Nereis diversicolor (polychaete)	whole	Pb	37	F	- NH_4OH (1M)/pH 11.6 - NH_4OAc (1M)/pH 7 - $(NH_4)_2C_2O_4$ (0.4M), $H_2C_2O_4$ (0.4M)/pH 3.3 - HOAc (25%)/pH 2.2 - HNO_3 (15M)/digestion (fresh sediment, < 100 µm; non-sequential)	Pb extracted with HNO_3 (r^2 = 0.54, log-log)	Luoma & Bryan 1982
	whole	Pb	4	F	- HCl (1M) (fresh sediment, < 100 µm)	Pb extracted with HCl + percentage organic matter (r^2 = 1.00); Pb extracted with HCl (r^2 = 0.90)	Bryan 1985

* N = number of sites.
** Study type: F = field survey.

be a fruitful area for research

- in both freshwater and marine systems, lead levels in benthic invertebrates are normally better related to lead concentrations in one or more relatively easily extracted fractions, present in the fine sediments, than to total lead concentrations
- for benthic invertebrates, lead bioavailability decreases in the presence of appreciable concentrations of amorphous iron oxyhydroxides; predictions of lead levels in invertebrates are improved when the lead concentration extracted from the sediment is normalized with respect to the iron oxyhydroxide content of the sediment
- this dependence of lead accumulation on sediment characteristics does not, however, imply that the main route of lead accumulation is necessarily via ingestion of particulate material; it can be explained by adsorptive control of the dissolved lead concentration in the interstitial water to which the organism is exposed (Eq. 4).

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7. SPECIATION OF ORGANOLEAD IN THE ENVIRONMENT AND METHYLATION OF LEAD

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Organolead Compounds in the Aquatic Environment

The sources of organolead compounds in the environment are mainly anthropogenic, although methylation processes through biotic and abiotic pathways cannot be completely ruled out. There are numerous organolead compounds known, but the most important and widely used ones are the tetraalkylleads, also known as lead alkyls (R=Me,Et), used as antiknock additives in gasoline; these are the most important source of lead pollution in the environment. There are other uses of alkyllead compounds, but in much lesser quantities. The important uses of organolead compounds are shown in Table 1.

Table 1.

Major uses of selected organolead compounds.

Tetraalkyllead - antiknock additives
    fumigants
    filling gas for Geiger counters
    alkylating agent in manufacturing of organomercurials
    catalyst in polymerization reactions
    stabilizers for polyvinylchloride
    wear-reducing additives in lubricating oils

Trialkyllead, dialkyllead -
    insecticides, fungicides, bactericides
    antifouling agents in paints
    rot-proofing for cotton and woollen fabrics
    wood preservatives

Organolead compounds from automobile emissions and industrial wastes are carried by rain, atmospheric fall-out and river runoff. Tetraalkyllead compounds are slowly degraded to trialkyllead, dialkyllead and Pb(II) by ultraviolet light. Their overall degradation is slow, with half-lives ranging from 3 h for Et_4Pb to over 60 d for Me_3PbCl.

Tetraalkylleads are lipophilic compounds and are accumulated rapidly from water by fish. In a recent study, the highest concentrations were found in the lipid layer of the intestine of rainbow trout (Wong et al., 1981). The dialkyllead and trialkyllead, although ionic in nature, are also concentrated in fish (Chau et al., 1985) and in clams (Chau et al., unpublished data, 1985).

Speciation of Alkyllead in Environmental Samples

For obvious reasons, methods for the determination of alkyllead compounds have been developed mostly for the molecular tetraalkyllead in the atmosphere. Much less attention has been given to the existence of the ionic dialkyllead and trialkyllead in the environment. Lack of analytical methods is at least one of the reasons for such discrepancies.

There are two major classes of alkyllead of environmental concern. One is the volatile tetraalkyllead (R=Me,Et), which includes the widely used tetramethyllead and tetraethyllead antiknocking additives in gasoline. The tetramethyllead could also be a product of natural methylation. These compounds are non-polar and are insoluble in water. They are accumulated in the lipid tissues of living organisms, adsorbed onto particulates or volatilized into the atmosphere. In the second class are the ionic alkylleads, such as dialkyllead and trialkyllead (R=Me,Et), which are hydrophilic and present in solution as salts. No monoalkyllead compounds are known to occur due to their extreme instability. The determination of ionic alkyllead compounds has been historically difficult because of their resistance to extraction by any organic solvents. Chemical behaviours among the methyl and ethyl derivatives of the dialkyl- and trialkylleads are exceedingly similar, such that many methods simply cannot provide the specificity for their respective identification.

Available methods are mainly spectrophotometric or atomic absorption spectrometric techniques coupled with chemical manipulations to achieve speciation. Mostly they lack the required specificity or sensitivity for environmental analysis. Thus environmental occurrence of the various tetraalkyllead species was not determined until 1979 (Chau et al., 1979). Methods for speciation of the various ionic alkyllead compounds in water have only recently become available (Chau et al., 1983).

Tetraalkyllead

Tetraalkyllead species include the two major lead alkyls and their mixed alkyls, namely:

Tetramethyllead, Me_4Pb

Trimethyl ethyllead, Me_3EtPb

Dimethyl diethyllead, Me_2Et_2Pb

Methyl triethyllead, $MeEt_3Pb$

Tetraethyllead, Et_4Pb

Tetraalkyllead compounds are molecular and non-polar and are readily extractable by non-polar solvents. They are volatile and can be directly chromatographed after being cryogenically trapped. The most elegant and sensitive technique is no doubt the gas chromatography - atomic absorption spectrometry technique (GC-AAS), which is not only element-specific (specific to lead-containing compounds), but also identifies the alkyl groups in each compound by virtue of the chromatographic retention times (Chau et al., 1976; DeJonghe et al., 1980). By this technique, tetraalkyllead in air can now be speciated to molecular forms with sensitivity to the 0.1 ng m^{-3} level (DeJonghe et al., 1981).

The determination of tetraalkylleads in water represents only the transient concentrations, as these compounds are not soluble in water, and their aqueous solutions are only unstable physical suspensions. They will eventually partition into the lipids of living organisms or be adsorbed onto particulates, or volatilize into the atmosphere. In areas of alkyllead contamination, such as the St. Clair River and St. Lawrence River, tetraalkyllead species can be found in water, surface microlayer, sediment and aquatic biota. Chau et al. (1979) developed a specific method for determining all five tetraalkyllead compounds in natural water, sediment and fish. In this method, tne samples are extracted with hexane in the presence of EDTA and directly analysed by a GC-AAS technique. Detection limits are, respectively, 0.5 µg L^{-1} for water, 0.01 µg g^{-1} for sediment and 0.025 µg g^{-1} for fish. Using these methods, miscellaneous tetraalkyllead compounds have been found in fish and sediment samples in several locations in Ontario (Chau et al., 1980).

Dialkyllead and Trialkyllead

The dialkyl- and trialkyllead species are ionic compounds. They are mainly decomposition products of tetraalkyllead. The typical compounds are:

Dimethyllead, Me_2PbX_2; diethyllead, Et_2PbX_2

Trimethyllead, Me_3PbX; triethyllead, Et_3PbX

The major difficulties in their speciation have been (i) the isolation of the ionic alkyllead species from sample matrices without changing the original chemical forms, and (ii) the availability of a specific technique for their individual determination. The ionic characteristics of R_2PbX_2 and R_3PbX

do not allow the quantitative extraction of them by any organic solvents. However, in the presence of NaCl, Et_3PbCl can be extracted from aqueous medium with benzene (Bolanowska, 1957), and determined as dithizonate after acid back extraction and mineralization. This method was claimed to be specific for R_3PbX in the presence of R_4Pb, R_2PbX_2 and Pb(II). The specificity, however, depends solely on the chemical manipulations and isolation, and not on the final determination. Subsequent improvements have been made in the analysis of Pb species in sediment with the addition of excess NaCl and inorganic Pb(II) to enhance the release of alkyllead from sediment (Potter et al., 1977), followed by thin-layer chromatography (TLC) and a spectrophotometric method using a specific reagent, 4-(2-pyridylazo)-resorcinol (PAR), for R_2PbX_2 compounds. However, recoveries for the two dialkyllead compounds are still not satisfactory.

Further improvements of extraction of ionic alkyllead species have been reported in a study with biological samples by Birnie and Hodges (1981), who used toluene in an iodide/chloride medium. The addition of sodium benzoate enhanced the extraction of dialkyllead species. The recovery of R_3PbX and Et_2PbX ranged from 70 to 90%, but that for the Me_2PbX_2 species ranged from 10 to 40%, depending on the nature of the biological samples. In this method, the final analysis was carried out in a back extraction solution of 1% HNO_3 in the presence of EDTA. R_3PbX and R_2PbX_2 were measured by an anodic stripping voltammetric method with a sensitivity of 0.01 $\mu g\ g^{-1}$ for fish. The method is relatively specific for the dialkyl- and trialkylleads as a class, but it cannot identify the alkyl groups in the compounds. Almost concurrently, an electrochemical method, based on selective extractions of the alkyllead species, for consecutive determination in natural waters of Me_4Pb, Et_4Pb, Me_3Pb, Et_3Pb,

Me_2Pb, Et_2Pb and Pb(II), was reported by a separate research group (Columbini et al., 1981) with detection limits from 0.04 to 0.08 µg L^{-1}. The method, however, is not a direct speciation method. Its specificity depends on a series of chemical separations and calculations by difference. The method is lengthy and easily subject to contamination and errors.

Gas chromatographic methods using various detectors have also been reported. In all these methods, the trialkyllead is first extracted in a saturated NaCl medium by a solvent prior to chromatography. A detection limit of 10^{-10} g was claimed for Me_3Pb and Et_3Pb (Hayakawa, 1971). A similar method with capillary column and microwave plasma detector achieved a detection limit of 10-30 µg L^{-1} of Et_3Pb for water (Estes et al., 1982). Flame ionization detectors have also been used in gas chromatography, but sensitivity is relatively poor and the method is not at all suitable for environmental work (DeJonghe and Adams, 1983).

All the above methods suffer either from lack of sensitivity and selectivity or from limited speciation capability. Recently, a breakthrough in the analysis of ionic alkyllead species has been achieved by using a chelating agent, sodium diethyldithiocarbamate (NaDDTC), to extract in their authentic forms all the ionic alkyllead species including Pb(II) from solution. The alkyllead and Pb(II) are butylated with n-butyl Grignard reagent to the corresponding tetraalkylated forms, R_nPbBu_{4-n} and $PbBu_4$, all of which can now be quantified by a GC-AAS method. The molecular and covalent tetraalkyllead species, if present in the sample, are also extracted, but they are not affected by the butylation reaction (Chau et al., 1983). Environmental occurrence of R_2Pb and R_3Pb has been observed for the first time in fish, sediment, water and surface microlayer in the St. Clair and St. Lawrence Rivers, with a detection limit of 0.1 μg L^{-1} in water (Chau et al., 1984, 1985). At the same time, a method using dithizone to isolate the ionic alkyllead from a variety of media including water and biological materials, and phenylation to convert them to volatile derivatives, was published (Forsyth and Marshall, 1983). The presence of dialkyllead and trialkyllead species in herring gull muscle and eggs has been confirmed (Forsyth and Marshall, 1986). Without these techniques, the fate and pathways of alkyllead in the environment cannot be properly assessed.

Subsequent modifications of the above chelation/extraction and GC-AAS method have been published, with improved sensitivity (Chakraborti et al., 1984; Harrison and Radojevic, 1985). With 500 mL of water, ionic alkyllead can be detected at nanogram per litre concentrations.

Digestion of biological samples without breaking down of the chemical forms has also been overcome by using a tissue solubilizer, tetramethylammonium hydroxide (TMAH). This reagent dissolves fish tissues, aquatic weeds, etc., without the necessity of rigorous heating, and releases the protein-bound alkyllead and inorganic lead compounds intact without rupturing any lead-carbon bonds. These compounds are now ready for extraction and subsequent determination (Chau et al., 1984).

Thus, a sensitive and specific method for complete speciation analysis of all molecular and ionic alkyllead compounds (R=Me,Et) is now available for environmental studies. A typical GC-AAS chromatogram showing the speciation of five tetraalkylleads, four ionic alkylleads and inorganic Pb(II) is illustrated in Figure 1.

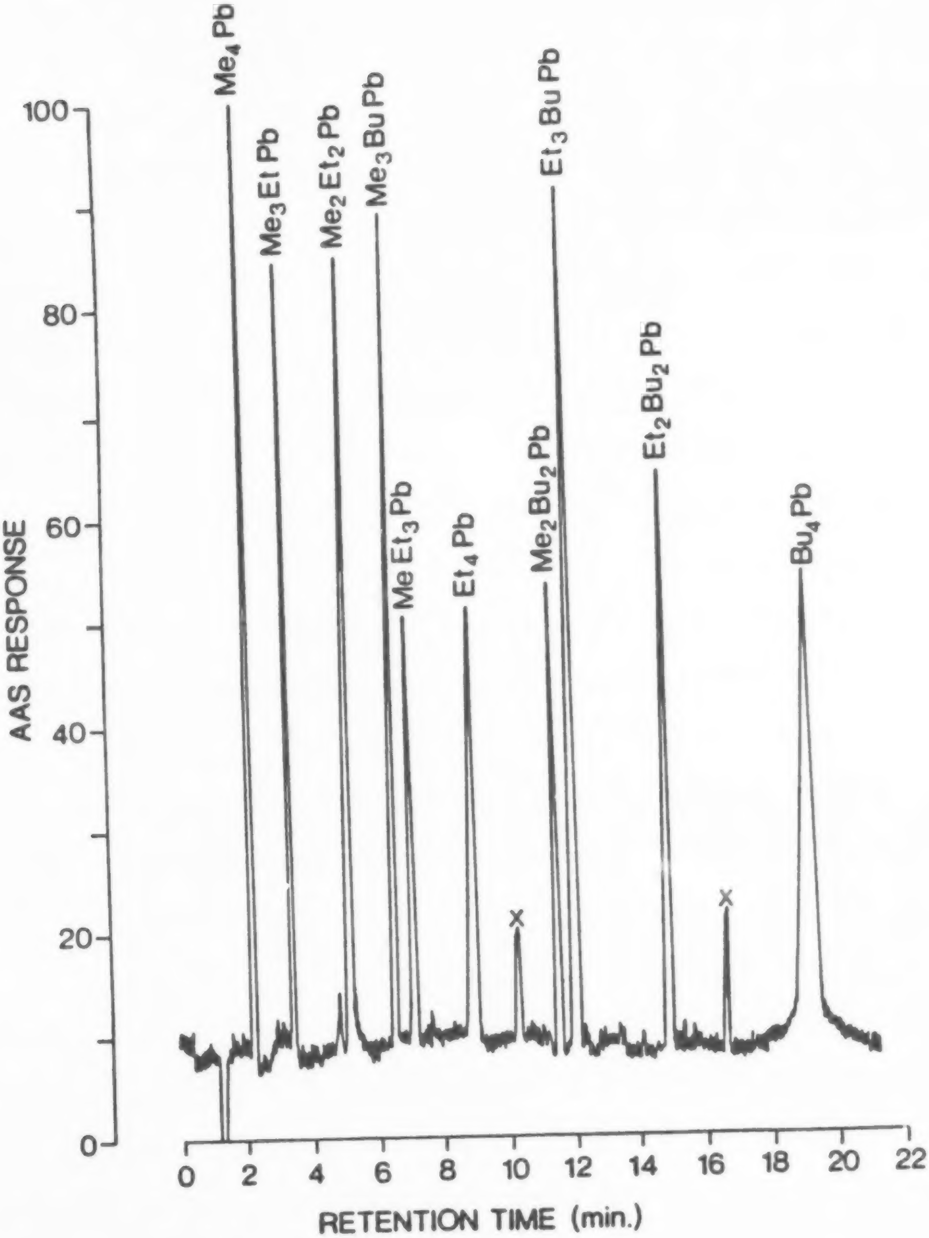

Figure 1. Gas Chromatography-Atomic Absorption Chromatograms of Five Tetraalkyllead Compounds (10 ng each); four butyl derivatives of Dialkyl- and Trialkyl-lead (8 ng each) and Pb (II) (15 ng).

X - Unidentified Lead Compounds.

Lead Methylation

Methylation of Pb(II) compounds has been and still is controversial since its first report in 1965 (Wong et al., 1975). There are only a few international groups interested in this problem. None of these research groups, however, has been able to produce any affirmative and unequivocal results on Pb(II) methylation in the environment. The following is a summary of research work on Pb(II) methylation.

Summary of publications on Pb(II) methylation:

	Positive results	Negative results
1975	Wong et al. (1975)	Wong et al. (1975) Jarvie et al. (1975)
1976	Schmidt and Huber (1976)	
1977	Dumas et al. (1977)	
1978	Huber et al. (1978)	Wood and Craig (1978)
1980	Ahmad et al. (1980) Thompson and Crerar (1980) Craig (1980)	
1981	Jarvie and Whitmore (1981)	Reisinger et al. (1981)
1982	Craig and Rapsomanikis (1982)	Snyder and Bentz (1982)
1984	Rapsomanikis et al. (1984)	

In contrast, methylation of Pb(IV) compounds is straightforward and has been agreed upon by all workers concerned, although there are still some arguments as to whether the processes are biotic (biological) or abiotic (chemical). From an environmental point of view, it is not crucially important whether the processes involved are biological or chemical.

The differences in conclusions on Pb(II) methylation seem to have been caused by the following discrepancies:

1) Differences in detection limits of methods used in different studies. Those that found positive results used methods sensitive to nanogram quantities; those with negative results employed methods that detected microgram quantities. Pb(II) methylation, unlike Pb(IV) methylation, is a low-yield reaction.

2) Difference in strains of micro-organism used.

3) Difference in sediment composition.

4) Possibility of transmethylation. Alkylated lead compounds readily pass their alkyl groups to metals ions, e.g. Sn(II), Hg(II) (Chau et al., 1987). If these metals are present in the system, alkyllead may not be found.

The complexities and difficulties of investigations of biological methylation of Pb(II) under environmental conditions have been fully appreciated by workers in this area. Recent studies tend to focus on the chemical aspects of methylation through which it is hoped that some understanding of the mechanisms may be gained. Methylation of Pb(II) has been shown possible by methyl group donors in aqueous solution (Ahmad et al., 1980; Craig and Rapsomanikis, 1982; Rapsomanikis et al., 1984). With further knowledge of the chemical mechanisms and pathways involved, it is hoped that the mystery of lead methylation in the environment will soon be unveiled.

Summary

The sources of organolead compounds in the environment are mainly of an anthropogenic nature, although biotic and abiotic methylation reactions have been suggested as possible sources.

Ionic alkyllead compounds, namely trialkyllead and dialkyllead, are degradation products of tetraalkyllead under environmental conditions. Their existence in environmental materials was not known because of the lack of sensitive analytical techniques for their determination. Recently, a breakthrough in the determination of ionic alkyllead species has been achieved by extracting these compounds in their authentic forms with a chelating agent, sodium diethyldithiocarbamate (NaDDTC), from solution and from biological samples. After butylation of the extracted trialkyl- and dialkyllead to the corresponding tetraalkylated forms, R_nPbBu_{4-n}, (R=Me, Et), they have the appropriate volatility to be analysed by the GC-AAS technique. Triethyl-, diethyl- and tetraethyllead compounds have been found in water, surface microlayer, fish, sediment and macrophytes in areas near the lead alkyl production plants.

More and more chemical proofs are available to support the possibility of Pb(II) methylation in the environment, although the subject matter is still in a state of controversy.

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8. CYCLING OF LEAD INTO FOOD WEBS IN AQUATIC ENVIRONMENTS

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Introduction

Most of the lead in aquatic environments is associated with sediments and water; only a small proportion of the total quantity penetrates into food webs. However, that small proportion determines any adverse biological impacts which the metal may have, and determines the exposure to humans from aquatic sources. To assess the biological significance of lead in aquatic environments we must understand (i) processes that control the extent of lead transfer from major environmental compartments to food webs; (ii) how lead is distributed once it enters different types of food webs; and (iii) if simple measures such as sentinel species can be employed to assess cycling of biologically available lead. This paper reports on the present state of knowledge concerning these questions. It also addresses the question of interactions between lead and cadmium in aquatic organisms.

Lead Transfer to Food Webs

The transfer of lead from water and sediments into food webs is not a simple function of lead concentration in the environment. Chemical speciation in solution affects the accessibility of lead to organisms, as does the chemical partitioning of lead in sediments. Laboratory studies have shown that lead uptake by fish is reduced when dissolved organic carbon concentrations are elevated (Wiener and Giesy, 1979), when phosphate concentrations are increased (Freedman et al., 1980) or when pH is elevated (Merlini and Pozzi, 1977). Statistical studies in natural systems have shown reduced concentrations of lead in organisms living in systems where sediments are high in organic carbon (Schierup and Larsen, 1981) or high in amorphous iron oxides (Luoma and Bryan, 1978; Tessier et al., 1984). Similarly, in areas of moderate lead enrichment, concentrations in organisms can be very high if organic carbon or amorphous iron oxide concentrations in sediments are low. Table 1 (data taken from Luoma and Bryan, 1978) shows lead concentrations in sediments and in the sediment-ingesting bivalve Scrobicularia plana from several estuaries in southwest England. Concentrations in the animals predicted from a correlation with the ratio Pb/Fe-amorphous in sediments of 38 stations from 17 estuaries in southwest England are also shown, along with iron concentrations in sediments (Luoma and Bryan, 1978). Data from the Looe estuary illustrate that high concentrations of lead occurred in S. plana in coincidence with moderate lead enrichment and sediments relatively poor in iron, while little lead was accumulated in animal tissues from the heavily

Table 1.

Concentration of Pb and Fe in sediments (1 N HCl extraction) and Pb in the deposit-feeding bivalve Scrobicularia plana, compared with Pb predicted to be in S. plana from the ratio Pb/Fe in sediments in Luoma and Bryan (1978). All values in μg g^{-1} dry weight.

Estuary	Sediment Pb	Sediment Fe	Observed S. plana	Predicted S. plana
Axe	25	6525	8	9
Elorn	71	7099	31	34
Looe	63	2104	165	121
Humber	191	21000	22	28

enriched Humber estuary, in coincidence with high concentrations of iron in sediments. Such results indicate that in some environments lead may penetrate benthic food-chains much more efficiently than in others, and that the efficiency of transport into the biota may be linked to the geochemical characteristics of the environment. However, we are only beginning to understand the significance of specific geochemical effects; thus studies of lead in the food webs themselves remain the most reliable means of identifying environments enriched with biologically available lead.

Lead Distribution in Food Webs

Important questions in assessing lead distribution in food webs include (i) does lead accumulate to higher concentrations at higher trophic levels? (ii) are any other trophic consistencies evident within food webs? and (iii) what species might be the major vectors to humans from a lead-contaminated environment? Of course the answers to these questions might vary between freshwater and estuarine/marine environments.

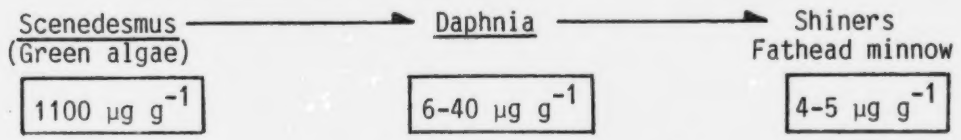
Freshwater Systems

Concentrations of lead in the very simple food-chain of a biological waste-water treatment plant (Tarifeno-Silva et al., 1982) clearly showed that lead concentrations decline at higher trophic levels (Table 2). Very high concentrations of lead were evident in phytoplankton (more than 0.1% of the dry tissue mass of these organisms was lead). However, concentrations in Daphnia that fed upon the microscopic plants were more than 20-fold lower than in the plants, and concentrations were another order of magnitude lower in both species of fish within the system. The concentrations of lead in the fish in this system were as high as recorded in lead-contaminated environments (e.g. Brown and Chow, 1977; Roth and Horning, 1977; May and McKinney, 1981).

Table 2.

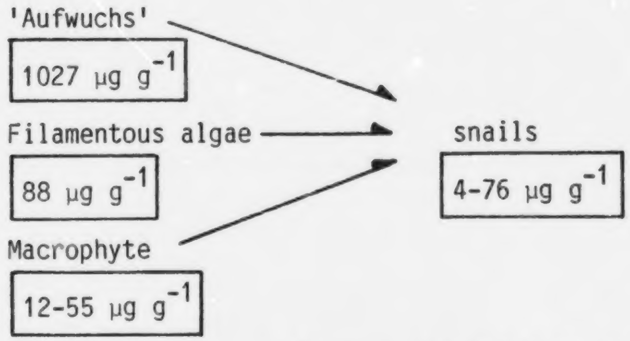
Concentrations of lead in several different freshwater food-chains in lead-contaminated environments. Some results are consistent with biominification of the metal; others are not.

Food-chain in Biological Wastewater Treatment Plant


Scenedesmus
(Green algae)
1100 µg g^{-1}
Daphnia
6-40 µg g^{-1}
Shiners
Fathead minnow
4-5 µg g^{-1}

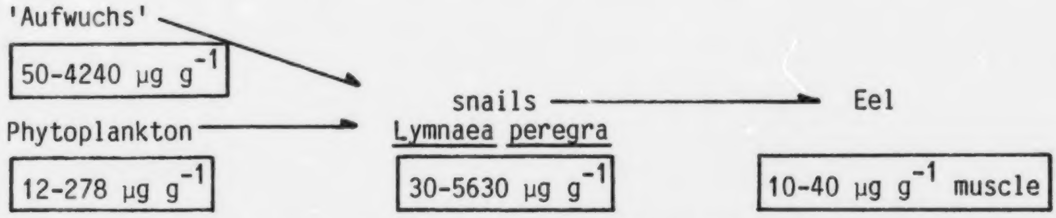
(Tarifeno-Silva et al., 1982)

Freshwater Lake


'Aufwuchs'
1027 µg g^{-1}
Filamentous algae
88 µg g^{-1}
Macrophyte
12-55 µg g^{-1}
snails
4-76 µg g^{-1}

(Newman and McIntosh, 1982)

Ullswater (Lead Mining)


'Aufwuchs'
50-4240 µg g^{-1}
Phytoplankton
12-278 µg g^{-1}
snails
Lymnaea peregra
30-5630 µg g^{-1}
Eel
10-40 µg g^{-1} muscle

(Denny and Welsh, 1979; Everard and Denny, 1984)

Distributions of lead in natural freshwater food webs are more complex than indicated in the artificial wastewater treatment system. In natural systems several types of primary producers occur, and precise feeding relationships are not always well known. For example, study of a lead-contaminated lake (Newman and McIntosh, 1982) showed that different types of plants may differ in lead concentration by more than an order of magnitude (Table 2). The highest concentrations occurred in 'aufwuchs', the community of periphyton, bacteria and fungi that occurs attached to solid surfaces. (One of the difficulties in sampling 'aufwuchs' is separating living material from fine-grained inorganic material trapped by the organisms. Therefore these elevated concentrations also may reflect lead contamination on fine-grained particulates.) Concentrations of lead among four species of snails from the lake were more than 10-fold lower than observed in the 'aufwuchs' community. However, the snail species with the highest mean lead concentration (76 $\mu g\ g^{-1}$) were contaminated as much as filamentous algae or macrophytes, two other possible food sources, while the snail species with the lowest mean concentration of lead (4 $\mu g\ g^{-1}$) was less contaminated than any species of plant. In the Ullswater mining region of Great Britain, lead concentrations in the snail Lymnaea peregra were as high as observed in the local 'aufwuchs' community, and higher than that found in phytoplankton (Denny and Welsh, 1979; Everard and Denny, 1984). Concentrations in eel flesh, however, were considerably lower than in the other organisms (again, this appears to be typical for fish).

Thus, in contaminated lake environments, exceptional lead concentrations can be found in 'aufwuchs' and some phytoplankton. Concentrations in some low consumers can equal those in even the most contaminated plants, while considerably less lead accumulates in other low consumer species. Although biomagnification at the first trophic step is not evident in these systems, neither do all plant-grazing species efficiently exclude lead. All studies indicate that fish exclude at least inorganic lead from their muscle tissue more efficiently than do many other species.

Fish are a primary vector of lead from freshwater environments to humans. Fish flesh from contaminated freshwater environments may exceed the standard for human consumption by as much as five-fold, and equal the concentrations found in otherwise uncontaminated food from lead-soldered cans (Settle and Patterson, 1980). Nevertheless, these concentrations are considerably less than those found in freshwater plants and at least some freshwater invertebrates.

The dominant components of the lower trophic levels in streams and rivers often differ substantially from those of lakes. We have recently begun a study of lead concentrations in sediments and three species of benthic insects from the Clark Fork River in Montana. This river originates (as Silver Bow Creek) in the middle of a very large copper mining/smelting district. One of the important contaminants originating from the area is lead. Concentrations of lead in fine-grained (less than 16 μm) sediments 40 km from the smelter were 191 μg g^{-1}, declining to 105 μg g^{-1} 80 km from the smelter (Table 3). Because of lead input from a contaminated tributary at 88 km, concentrations in the sediment remained at 110 μg g^{-1} at 95 km, then declined to 62 μg g^{-1} at 178 km. Background concentrations in uncontaminated tributaries averaged 10 μg g^{-1}, but lead concentrations in the Clark Fork remained more than 2 times greater than this 365 km downstream (the farthest downstream that samples were collected).

Table 3.

Concentrations of Pb ($\mu g\ g^{-1}$) in sediments and tissues of insect larvae collected various distances from the Butte/Anaconda mining/smelting district on the Clark Fork River, Montana.

	Distance (km) from the smelter				
	40	80	95	178	Tributary
Sediment	191	111	110	62	10
Caddisfly	20±4	5±1	12±4	4±1	<4
Stonefly (grazer)	np*	np	16±3	4±1	<4
Stonefly (predator)	np	np	<4	<4	<4

* np = not present.

The three insect larvae that were collected were a web-spinning detritus feeder (a Hydropsychid caddisfly larvae), a detritus-feeding stonefly (a Pteronarcid) and a predaceous stonefly (a Perlid). Feeding habits were as reported by Merritt and Cummins (1978). Twenty to forty individuals of each species were analysed at each site. The animals were allowed to purge their digestive tracts for 2-6 h after collection, frozen for storage and dissolved in a reflux of concentrated nitric acid before analysis by flame atomic absorption spectrophotometry. Because our laboratory did not meet ultra-clean criteria necessary for ultra-low-level lead analyses (Settle and Patterson, 1980), tissue concentrations less than 4 $\mu g\ g^{-1}$ (based upon tissue mass samples of 0.3-0.5 g) were considered below background. All concentrations in insects from uncontaminated tributaries were below this detection limit, but in the Clark Fork lead concentrations in the insects usually were well above background. Concentrations in the caddisfly larvae dropped fourfold and threefold, respectively, over the two river reaches where sediment concentrations declined less than twofold (40-80 and 95-178 km). Concentrations in the detritus-feeding stonefly larvae also fell much more rapidly than concentrations in sediments where the animals were present and lead was detectable (95-178 km). Concentrations of lead in the predaceous stonefly larvae did not exceed the detection limit at any station.

This study again suggested biominification of lead at the trophic level of a predator. In general, concentrations in the organisms were also very low compared with those in sediments, and declined down-river more rapidly than those in sediments. Thus the biological availability of lead appeared to decline much faster than its concentration in sediments, at least in this specific river, and for the specific species considered.

Marine and Estuarine Environments

Amiard et al. (1982) conducted a thorough study of lead in the food web of the uncontaminated (25 $\mu g\ g^{-1}$ in sediment) Loire estuary in France (Figure 1). In agreement with the results observed in fresh waters, they found the lowest lead concentrations in more highly evolved, upper-trophic-level organisms (fish and larger crustaceans such as crabs and lobster). Higher concentrations were evident in some secondary consumers (both zooplankton and filter-feeders), and the highest concentrations occurred in organisms that ingest sediments (deposit-feeding molluscs and polychaetes). Such conclusions also generally hold true in studies of more contaminated environments. Concentrations of lead in excess of 10 $\mu g\ g^{-1}$ were not observed in any surveys of large crustaceans and fish (e.g. Bryan et al., 1985), even in the most contaminated environments. (It should be noted that inorganic lead is the source in all such studies, and that trophic transfer efficiency may differ if the source is organic lead (Hodson, p. 203.) However, very high concentrations of

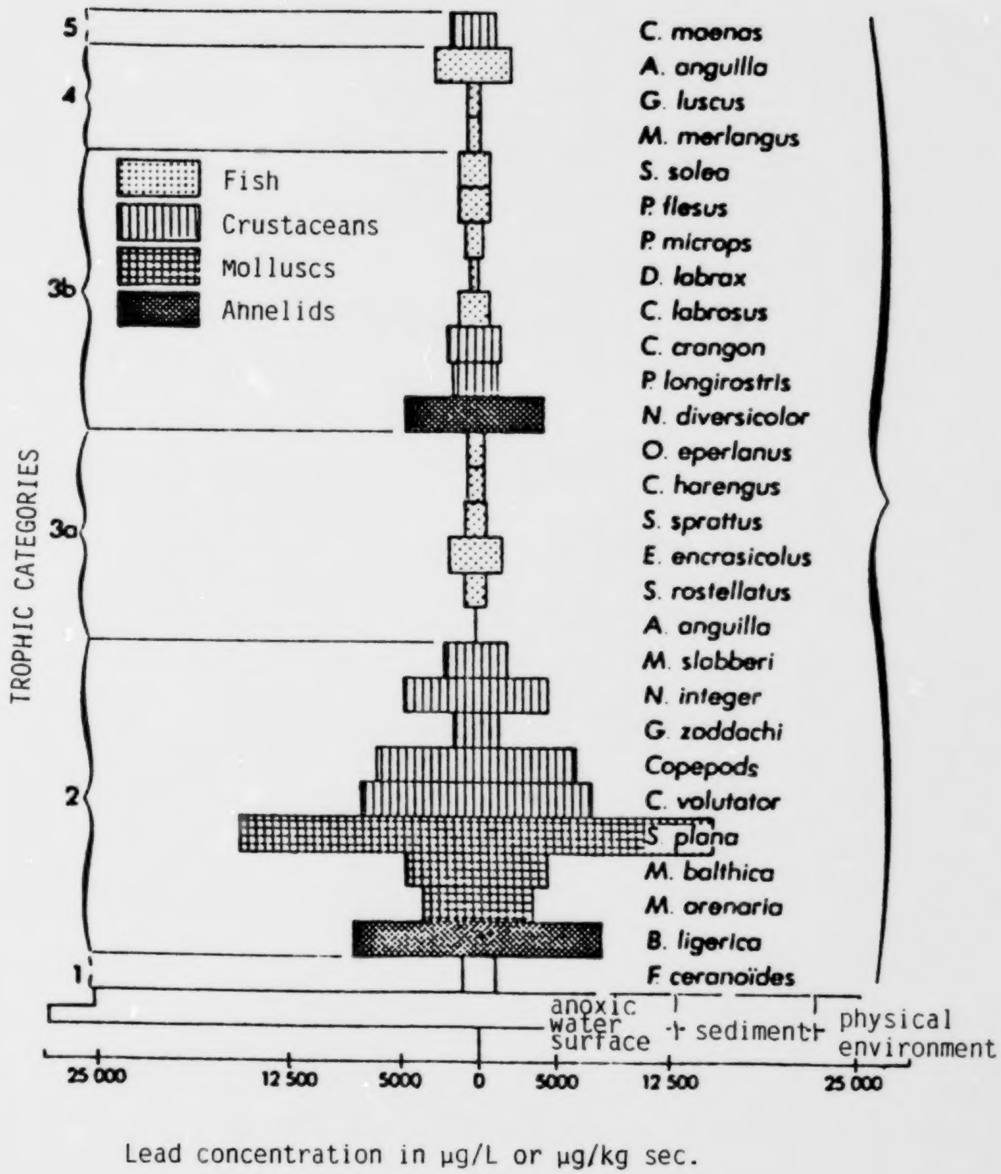


Figure 1. Concentrations of Lead in the Tissues of Organisms from the Food Web of the Loire Estuary in France.

SOURCE: Amiard et al., 1982.

lead can occur in some primary producers, grazers, filter-feeders and sediment-ingesting organisms.

The differences among the species that accumulate lead most efficiently are best illustrated in extensive surveys conducted by Bryan and co-workers (Bryan and Gibbs, 1983; Bryan et al., 1980, 1985) in more than 100 estauries in Great Britain, including areas of mine waste, industrial and domestic contamination. Table 4 shows maximum and minimum lead concentrations observed in several species of grazers, filter-feeders, deposit-feeders and macroalgae in those surveys. In contaminated environments, limpets and snails (both grazers) contained up to 30 $\mu g\ g^{-1}$ lead, some filter-feeders (mussels and cockles) hundreds of micrograms per gram and some deposit-feeders thousands of micrograms per gram. Two notable exceptions were oysters and the deposit-feeding clam Macoma balthica. Although similar in feeding habits to mussels, the highest concentration of lead observed in filter-feeding oysters was 12.5 $\mu g\ g^{-1}$, in contrast to observations of up to 530 $\mu g\ g^{-1}$ in mussel tissue. The deposit-feeder M. balthica is ecologically very similar to Scrobicularia plana. However, in contaminated environments, S. plana reached concentrations of several thousand micrograms per gram, while the maximum concentration ever observed in M. balthica was 60 $\mu g\ g^{-1}$.

From the above, it appears that unknown factors specific to the individual species can be as important in determining lead concentrations in organisms as trophic relationships. Although some generalizations are possible, in contaminated environments lead concentrations may differ among some species by orders of magnitude within feeding types. This also means that vectors to humans will vary in significance in such situations. Concentrations of lead in soft-shell clams from a severely lead-contaminated environment may approach

Table 4.

Ranges of Pb concentrations in ($\mu g\ g^{-1}$) observed in species from several different feeding guilds among estuaries of Great Britain (Bryan et al., 1985).

GRAZERS

Organism	Pb
Snails	
Littorina littorea	0.5-30
Limpet	
Patella unlgata	0.4-30

FILTER-FEEDERS

Organism	Pb
Mussels	
Mytilus edulis	1.7-530
Cockles	
Cerastoderma edula	0.4-371
Oysters	
Crassostrea virginica Ostrea edulis	0.3-12.5
Soft-shell clam	
Mya arenaria	3.0-2222

DEPOSIT-FEEDERS

Organism	Pb
Clam	
Macoma balthica	2-61
Clam	
Scrobicularia plana	8-3000
Polychaete	
Nereis diversicolor	0.2-1190

PRIMARY PRODUCERS
Sorfjorden (Melhuus et al., 1978)

Organism	Pb
Fucus vesiculosus	12-288
Ascophyllum nodosum	4-105
Enteromorpha	17-301
Chorda filum	15-130

or exceed those of some very significant better-known sources (e.g. newspaper; dirt contaminated with paint chips), and may exceed concentrations in such well-publicized sources as food from lead-soldered cans, by nearly three orders of magnitude. Mussels, seaweed and cockles could also be very significant vectors from such environments. In contrast, human exposures to lead from oysters taken from a contaminated environment would be comparable to the lower exposures expected from fish.

Usefulness of Indicator Species

Although differences occur among species in ability to accumulate lead, it appears that lead contamination is evident throughout a food web when it occurs (Tables 2 and 5). Concentrations of lead in all species increase where more biologically available lead is present. Therefore measurement of lead concentrations in one species could be sufficient to qualitatively indicate whether lead contamination occurs, in general, in the food webs of that environment. The sensitivity of such a comparison, of course, will be determined by the ability of the chosen 'sentinel' species to accumulate lead. The soft-shell clam Mya arenaria, the mussel Mytilus edulis or the clam Scrobicularia plana are sentinel species that would allow maximum differentiation among environments of differing lead contamination. If the potential maximum and minimum concentrations of lead in such species can be established from extensive field studies, a perspective concerning the relative degree of contamination of the food web compared with other environments may be possible from such an analysis.

The Mussel Watch programme (Farrington et al., 1983) demonstrates the usefulness of employing a benthic indicator organism (sentinel organism) if extensive data are properly collected. One interesting result of that

Table 5.

Concentrations of Pb (in µg g^{-1}) dry weight in species of different feeding guilds from three estuaries.

	Severn estuary	West Looe estuary	Isle of Man
Sediment	88	104	3200
DEPOSIT-FEEDERS			
Scrobicularia plana		189	3000
Macoma balthica	9	61	
Nereis diversicolor	3	25	
FILTER-FEEDERS			
Mytilus edulis		45	198
Cerastroderma edule		5	371
Mya arenaria			2222
GRAZERS			
Littorina littorea	4	17	
Patella vulgata	10	30	
SEAWEED			
Fucus vesiculosus	3	17	

programme was the comparison of concentrations of lead in the tissues of mussels at 29 stations from north to south along the west coast of the United States. Concentrations in animals throughout southern California were consistently more than fivefold greater than in animals from the northern coast. High values on the southern California coast ranged from 6.5 to 14 µg g^{-1}. In contrast, lead concentrations were less than 1.6 µg g^{-1} at all 15 stations north of the Farallon Islands in central California. This strongly suggested that lead inputs from a large urban complex such as Los Angeles can be detected over a widespread area in food webs in associated marine environments.

Compared with the studies of Bryan et al. (1985), however, the highest of the concentrations in the southern California mussels were only 5% of the concentrations observed in mussels from severely contaminated lead mining regions elsewhere in the world. Even so, the concentrations in southern California did exceed standards for lead in human food.

Cadmium/Lead Interactions

An additional question posed by the Commission was that of interactions between lead and cadmium. In my extensive survey of the concentrations of both elements reported in a variety of biota, it is very clear that no correlation between the occurrence of the two metals exists in any species among aquatic systems, and few correlations occur within most systems. This may be at least partly because of differences in the biological fate and processing of the two metals. Cadmium appears to accumulate more readily than lead in upper trophic levels (Di Giulio and Scanlon, 1985). Therefore some trophic differentiation of the metals probably occurs. Cadmium binds strongly to the sulphydryl residues of proteins, and accumulates within cells as metal-protein complexes (one such group of proteins, the metallothioneins, is particularly important in the intracellular binding of cadmium). Lead, on the other hand, accumulates on the exterior cells, at least in invertebrates, in granules rich in carbonate (probably as a lead carbonate precipitate). The result is that the accumulation patterns of lead and cadmium are markedly different (Marshall and Talbot, 1978), and a physiologically driven correlation between concentrations of the two metals does not occur. Finally, available evidence suggests that different geochemical processes control the biological availability of the two metals. Thus tissue concentrations of the two may not correlate, even if environmental concentrations do. In view of the above, a lack of correlation in concentration within aquatic organisms is not surprising.

Research Needs

Predicting the fate of lead in aquatic environments will depend ultimately on a quantitative understanding of the geochemical and physiological processes that determine the extent of lead transfer from its largest repository, the sediments, to aquatic food webs. Similarly, the biological significance of lead concentrations observed in organisms will not be clear until the link between lead bioconcentration and the physiological stress imposed by the metal is understood. We also must understand why lead concentrates so differently in species that are apparently ecologically similar. This may necessitate improving our understanding of lead transfer through food webs and of processes determining lead uptake from both food and water. At present, lead concentrations in several species of aquatic organisms could be used to aid the regulatory process. For example, biosentinels could be used to demonstrate which aquatic environments are more contaminated than others with biologically available lead. Some such ranking of environments might ultimately lead to criteria for lead contamination, if creatively employed. It must be recognized, however, that the ecotoxicological significance of tissue lead measurements, or a predictive link between the tissue lead concentrations and the quantity of lead discharged to an environment, cannot be established without improving our knowledge of the processes described above.

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9. THE EFFECTS ON AQUATIC BIOTA OF EXPOSURE TO LEAD

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Introduction

The effects of lead on aquatic biota have been extensively reviewed (Wong et al., 1978; Demayo et al., 1982; Hart, 1982; Hodson et al., 1984a). This paper will summarize major findings, review new information and examine the implications for Canada's aquatic ecosystems by reference to case studies. This paper does not consider aquatic mammals, birds, reptiles or amphibians, nor does it consider marine biota.

Since 'effects' of lead on aquatic biota are a function of both exposure and toxicity (assuming all effects are negative), both must occur in conjunction. However, the actual dose taken up from water, sediment, food and particulates can only be estimated, and will vary considerably with the characteristics of these media and with the physiological state of the exposed organisms. Therefore, much of this review will concern factors that affect exposure and ultimately the impacts of lead in aquatic ecosystems.

Toxicity

Algae

The acute toxicity of lead to algae encompasses a variety of responses, ranging from cell death to changes in enzyme activity. Since cell death is difficult to ascertain, most toxicity tests measure short-term changes in productivity (growth in biomass), as shown by turbidity, cell counts, chlorophyll 'a' or $^{14}CO_2$ uptake.

The levels of lead in water that are toxic to algae range from 10 to more than 100,000 μg L^{-1}. The cause of this variation is primarily the complexing capacities of the media used in toxicity tests. Complexing capacity refers to the non-covalent binding of lead to inorganic and organic substrates that make it unavailable for uptake by algal cells. Complexed lead may remain as suspended or dissolved material or it may precipitate. Therefore, toxicity tests at high cell densities, high concentrations of algal nutrients, high alkalinity or high dissolved organic carbon content will require large amounts of lead to 'titrate' the complexing capacity and provide sufficient 'free' lead for algal uptake and toxicity. The greatest toxicity of lead to algae (10 μg L^{-1}) was measured when complexation was minimized; the medium was Lake Ontario water with a low algal cell density, and no added nutrients.

While the toxicity of 'free' waterborne lead seems relatively constant, it is obvious that toxicity of 'total' lead is not. However, since most authors report toxicity on the basis of 'total' waterborne lead, all references to lead concentrations in this review will refer to total, unless otherwise stated.

Other factors affecting lead toxicity include the test species, temperature and form of lead. There are insufficient data to conclude which species or genera are uniformly the most susceptible, but tolerance of lead may be characteristic of algae that excrete polysaccharides and polypeptides which bind lead ions. The variation between species is very much less than the variation induced by water quality. Temperature has a complex effect; toxicity is enhanced at both extreme high and low temperatures. These thermal effects are not well defined nor is their mechanism understood, although they may arise from the interaction between thermal stress and changes in the rates of lead uptake and depuration.

Alkyllead compounds (Pb(IV)) are 2-20 times more toxic than inorganic Pb(II) under the same test conditions, although tetraethyllead must be photodegraded to triethyllead before its toxicity is evident; algae do not seem to metabolically de-ethylate tetraethyllead. The enhanced toxicity of alkylleads may be due to their increased lipid solubility relative to inorganic lead, a factor allowing more rapid penetration of cell membranes.

Invertebrates

The acute lethality of lead to aquatic invertebrates is also highly variable, ranging from 280 to 71,000 μg L^{-1} (Demayo et al., 1982). The causes of variation are the same as for algae. However, species variation is much greater, with small pelagic zooplanktons exhibiting greater sensitivity than aquatic insects, and about the same sensitivity as amphipods.

Chronic toxicity is usually expressed after exposure for a significant fraction of the organism's lifetime, or several generations. Chronic effects of total waterborne lead include elevated mortality rates ($>$ 19-260 μg L^{-1}), reduced growth rates ($>$ 100 μg L^{-1}) and impaired reproduction ($>$ 30 μg L^{-1}). While these are useful end-points for toxicity tests, Borgmann et al. (1978) introduced an ecologically more relevant parameter, 'biomass production rate'. These authors integrate the combined effects of mortality, growth and reproduction. Biomass production of zooplankton and snails approaches zero at waterborne lead concentrations of 100 and 48 μg L^{-1}, respectively.

A second very relevant response is phototaxis of zooplankton. Light triggers diurnal vertical migrations of zooplankton which transfer nutrients within a lake and affect feeding and survival of juvenile or small species of fish. Phototaxis of four Great Lakes zooplankton species was impaired at lead levels ranging from 3.8 to 10 µg L^{-1} (Hodson et al., 1984a).

Thresholds of toxicity are rarely seen with chronic studies of invertebrates--i.e. the longer the exposure, the lower the effective concentration of lead in water. The role of complexed metals in toxicity to invertebrates is also poorly understood, although there are indications that the unique feeding physiologies of some species may interact with complexation. For example, some invertebrates are more susceptible to metals complexed by amino acids than to free metals, simply because these organisms ingest dissolved organic material as a nutrient (George, 1980; Borgmann and Charlton, 1984). The complexing agent acts as a carrier which, when digested, releases metal to cause toxicity. The role of particulates as a transport mechanism for metals may also be important to filter-feeders.

There is also evidence that lead toxicity to copepods may be slightly enhanced by exposure to other metals, and that isopods develop tolerance in contaminated areas.

Fish

The toxicity of waterborne lead to fish is also affected by water quality; median lethal concentrations (LC_{50} values) range from 200 to 542,000 µg L^{-1}, depending upon alkalinity (inorganic complexation). However, the lethal concentration of lead is almost constant when expressed on a 'free' metal basis. The most sensitive family appears to be salmonids and the least centrarchids, although sensitivity within a family may also vary. The toxicity of alkyllead compounds to marine fish increases with the number of alkyl side-chains; the 96-h LC_{50} values for tetramethyl- and tetraethyllead were 50 and 230 µg L^{-1}, about 3600 and 700 times lower than the LC_{50} for inorganic lead under the same conditions (Maddock and Taylor, 1980). The toxicity of alkylleads to freshwater fish has not been adequately studied.

The sublethal responses of fish to lead mimic those of mammals. Chronic exposures induce anemia through impaired hemoglobin formation and accelerated mortality of red blood cells; compensatory erythropoiesis is often observed. Neuropathy due to the focal degeneration of spinal neurons causes a loss of colour control (melanophores disperse), muscle tonus and circulation in the caudal region, and deterioration of the fins and skin. Since muscle tonus is usually imbalanced bilaterally, the result is spinal curvature. Ultimately the animal is less able to swim, feed and reproduce, and becomes very susceptible to fungal and bacterial infections. The neuropathy impairs behaviour and learning, and causes teratogenesis through lead deposited in the egg during maternal development. The threshold level of waterborne lead causing these effects is about 5 $\mu g\ L^{-1}$, and toxicity increases with exposure concentration and time.

Other effects include histopathology in a variety of tissues, although spinal neuron damage has been observed only by electron microscopy. Various enzymes are inhibited, and there are recent reports of subtle changes in carbohydrate metabolism and ion regulation at low levels of lead exposure (Larsson et al., 1985).

Chronic toxicity of waterborne lead to fish is modified by the same factors that control acute toxicity. The threshold level (TL) of total waterborne lead causing neuropathy in rainbow trout (Salmo gairdneri) varies with alkalinity (A - inorganic complexation) according to the formula:

$$\mathrm{TL}\ (\mu g\ L^{-1}) = \mathrm{antilog}_{10}(0.6932 + 0.0064 \times A\ (mg\ L^{-1}))$$

Similarly, pH controls lead accumulation and, by inference, toxicity; accumulation and toxicity should double for each decrease of pH by 1.0 unit from a reference pH.

Brook trout (Salvelinus fontinalis) are more tolerant of lead exposure than rainbow trout because they accumulate less lead under the same conditions; this may be the basis for most species variations in sensitivity. Newly hatched fish are much more sensitive to neuropathy than are older fish, in part due to a greater rate of lead accumulation and to a rapidly developing central nervous system (CNS). Hence, rapidly growing fish develop neuropathy more quickly and to a great extent than do slowly growing fish. Diet is also important, both for overall health and resistance and for control of membrane permeability; fish on a high-calcium diet accumulate less lead than those on a low-calcium diet, independent of waterborne calcium levels.

The relatively large size of fish allows the application of diagnostic techniques for exposure and effects developed for human medicine. The levels of blood lead and erythrocyte δ-aminolaevulinic acid dehydratase (ALA-D) activity give a clear indication of lead exposure and biochemical response. Their measurement is a better indication of 'dose received' than are chemical assays of water, particularly where the levels of waterborne lead and complexing capacity vary over space and time. Their application to biological monitoring has been reviewed by Hodson et al. (1984c).

The levels of blood lead and ALA-D activity associated with neuropathy in laboratory tests provide a useful scale for estimating effects in the field. Hodson et al. (1984c) estimated that rainbow and brook trout would exhibit an increasing prevalence of neurotoxicity as ALA-D inhibition exceeded 50% or blood lead exceeded 300 μg L^{-1}. The latter value is similar to the estimated threshold for subclinical toxicity in humans. Variations in chronic toxicity are often associated with changes in availability and accumulation of lead, but there are no data to show whether toxicity of tissue lead varies with species. Hence, a conservative approach is to assume that all species will be adversely affected above 300 $\mu g\ L^{-1}$ blood lead.

Bioaccumulation

Toxicity of lead to aquatic biota implies uptake for internal effects. Algae concentrate lead up to 5750 $\mu g\ g^{-1}$ dry weight in contaminated waters, and bioconcentration factors (BCF = tissue concentration / water concentration) of 15-20,000 have been observed. Since dead algae precipitate to sediments, this is a major route for transfer of lead from water to sediments.

Invertebrates, particularly molluscs and insects, also accumulate high levels of lead, with BCFs ranging from 1000 to 8000 on a dry-weight basis (200 -1600 on a wet-weight basis, assuming 80% moisture). The highest concentrations are usually found in the exoskeleton and the lowest in the muscle (Stinson and Eaton, 1983). High levels of lead are accumulated by snails that graze on small organisms, but the level of contamination is a function of feeding habits (Newman and McIntosh, 1983). Because aquatic insects are relatively sessile, abundant and accumulate lead, they have been recommended as good monitoring organisms for integrating environmental levels (Nehring et al., 1979).

Fish accumulate lead rapidly in blood, equilibrium being achieved in 4-8 d; other tissues may take up to 20 weeks to equilibrate. Depuration occurs at a slower rate and by poorly known routes of excretion. The half-life for blood lead is about 4-8 weeks after short-term exposures, but it increases with exposure time, probably due to the slow release of lead from other tissue pools. The BCF for lead in fish is usually less than 1000 on a whole-body basis, but alkyllead compounds are concentrated up to 10 times more. Lead residues in fish muscle are generally low, ranging from 40 to 200 $\mu g\ kg^{-1}$ wet weight, but they may exceed 1000 $\mu g\ kg^{-1}$ in contaminated areas.

Laboratory studies with trout have suggested that waterborne lead is the primary cause of toxic effects in fish; food appeared relatively unimportant due to poor uptake. However, several recent studies create some doubt, and the question should be further investigated. Newsome and Piron (1982) observed spinal curvatures in zebra danios (Brachydanio rerio) fed commercial tropical fish food. The symptoms resembled those of lead poisoning, and were associated with lead levels in the food of 300-1000 $\mu g\ kg^{-1}$. Live diets (less than 100 $\mu g\ kg^{-1}$) caused no spinal curvatures.

Bottom-feeding fish, in particular suckers (Catostomidae), accumulate more tissue lead in contaminated ecosystems than do centrarchids feeding in the water column at the same location (Hodson et al., 1983; Ney and Van Hassel, 1983; Czarnezki, 1985). Both groups are exposed to the same levels of waterborne lead, but the suckers feed on organisms living in contaminated sediments. This situation is not as clear as the feeding studies, and is further confounded by the observation that species within the same family (e.g. brook and rainbow trout) accumulate waterborne lead at different rates under the same conditions. These results indicate that food composition, the form of dietary lead and species variations in digestion physiology and lead sensitivity should be investigated.

The bioconcentration factors of algae, invertebrates and fish suggest a negative biomagnification, i.e. lead concentrations are inversely related to trophic level. Field surveys confirm this observation; planktonic organisms usually contain higher levels of lead than larger organisms. The cause may be a positive relationship between lead absorption and surface-to-body-weight ratios, i.e. small organisms with a relatively large surface area absorb proportionally more lead for their weight than do large organisms.

Lead Effects in Real Ecosystems

The effects of lead on real ecosystems are usually predicted from laboratory tests, generally for reasons of cost and the narrowness of disciplines and mandates of aquatic toxicologists. However, as the above review indicates, lead toxicity is not absolute, but varies considerably with biotic and abiotic factors, primarily interacting through variations in exposure. Lead impacts will be a function of the distribution of lead in aquatic ecosystems and of the availability of that lead as controlled by environmental quality.

The distribution of lead has been reviewed for the Great Lakes (Hodson et al., 1984a), and provides a useful model; high levels would be expected near point sources (mining, smelting, manufacturing), diffuse sources (storm sewers, atmosphere) and environmental sinks (sediments, particularly in deep water with slow currents). Therefore, one should expect elevated levels of lead in aquatic biota adjacent to point sources, in inshore regions of lakes near diffuse sources and in benthos residing in contaminated sediments. Furthermore, the occurrence of alkyllead compounds should enhance the levels of lead in biota at a given level of exposure, whereas waters with a high complexing capacity should reduce lead accumulation and effects.

The observed effects should range from mild inhibition of enzyme activities of fish (particularly ALA-D) to complete elimination of biota. Many severe effects on individuals (e.g. neuropathy) may not be observable if they reduce survival, and organisms present at a site may be 'tough old survivors', unrepresentative of the general population. The following is a review of several 'case studies' of lead contamination to show whether lead exposure and effects do, indeed, occur in real ecosystems.

Wales

Lead effects on Welsh streams have been documented since the 1800s (England: Fifth Report of the Commissioners on River Pollution 1874, Vol. 1, pp. 11-12; in Jones, 1940). Silver, lead and zinc mines in Wales date back several hundred years and were closed about 1920. Mining destroyed several streams, primarily due to the toxic effects of dissolved lead and zinc leached from tailings from the mines themselves. Toxicity was aggravated by the smothering effects of tailings eroded from stream bank deposits, but galena grit (PbS) itself was not acutely toxic (Carpenter, 1924, 1925; Jones, 1940, 1958).

Some of these streams have recovered as contamination decreased, with increasing populations of aquatic invertebrates and epiphytic algae. However, four decades after mining ceased, fish have not returned to some rivers (e.g. R. Ystwyth) which remain barren and fishless for many miles. That the mines were the cause was shown by historical records of fisheries, the presence of healthy biota in tributaries and the rapid recolonization of rivers during periods of drought (reduced leaching). Toxicity cannot be blamed solely on the presence of lead since zinc occurs as a co-contaminant. However, fish were absent from rivers when waterborne lead exceeded 100 μg L^{-1}, levels that caused acute mortality of local fish species tested in water of similar quality.

Missouri

More modern mining has had similar impacts. In the 'Old Lead Belt' of Missouri, abandoned tailings are eroding into streams along with contaminated leachate. Lead levels of 5-20 μg L^{-1} in filtered (0.45 μm) water from the Big River downstream of eroding tailings exceed those of reference streams (less than 5 μg L^{-1}; Schmitt et al., 1984). Contaminated whole fish contained 9-18 μg g^{-1} wet weight compared with levels of 0.25 μg g^{-1} in reference fish (May and McKinney, 1981).

Suckers (Moxostoma duquesnei, M. erythrum, Hypentelium nigricans) had blood lead levels of 80 μg L^{-1} in reference streams, but averaged 630-1810 μg L^{-1} in the Big River (Schmitt et al., 1984). These same fish exhibited a 53-77% inhibition of erythrocyte ALA-D activity relative to reference fish, and levels of lead in the fillets (muscle) ranging from 0.38 to 0.79 μg g^{-1}, well in excess of reference levels of 0.07 μg g^{-1} and a recommended limit of 0.3 μg g^{-1} of lead in human diets (WHO, 1972).

Schmitt et al. (1984) did not observe any visible signs of lead intoxication in sampled fish, although it was clear that lead was both biologically available and biochemically active. The response of ALA-D could have been much greater had not fish contained elevated levels of blood zinc, a metal that activates ALA-D and decreases lead inhibition. Nevertheless, the presence of fish is not equal to 'no impacts' if fish migrate in from unaffected areas or if productivity is reduced. A reduction in biomass and species composition of benthic invertebrates has been reported in these areas, but there were no simultaneous studies of fisheries productivity.

The occurrence of lead in the edible portion of suckers was also confirmed by Czarnezki (1985). In streams of the nearby 'Tri-State Mining District' of Missouri, average levels of lead in fillets ranged from 0.13 to 0.88 μg g^{-1}, depending upon how far downstream of the source the samples were taken. Reference values averaged 0.06-0.12 μg g^{-1}. Levels of lead in the fillets of bass (Micropterus dolomieu) and long-eared sunfish (Lepomis megalotis) were much less, ranging from 0.05 to 0.39 μg g^{-1} in contaminated streams and 0.08 to 0.09 μg g^{-1} in control streams. These data illustrate the difference between benthic feeding fish (suckers) and those feeding primarily in the water column (centrarchids).

Sweden

Lead mining in north-west Sweden has polluted two lakes, Laisan and Aisjaure. Larsson et al. (1985) summarized a series of studies that demonstrated 10-70 times higher levels of lead in the liver of whitefish (Coregonus spp.) from contaminated lakes relative to those from a reference lake. At the time of the study, waterborne lead levels were 0.5-4.5 and 0.5 μg L^{-1} in the affected and reference lakes, respectively. The lead-exposed whitefish demonstrated an ALA-D inhibition of 88% and disturbed ion and glucose regulation. These effects were reproduced in the laboratory by exposures of fish to as little as 5 μg L^{-1} Pb. Population and ecosystem effects were not assessed.

Nova Scotia

Lead mining has had similar impacts in Canada. A lead mine adjacent to the Salmon River in southern Cape Breton is associated with levels of lead in sediment of up to 1.8% (18,000 μg g^{-1}); zinc (63-1000 μg g^{-1}), cadmium (0.2-32 μg g^{-1}) and copper (1.7-23 μg g^{-1}) were less elevated (Westlake and Smith, 1981). Contamination was greatest in a small cove adjacent to the mine, about 75 m long by 20 m wide; it may be due, in part, to natural erosion of soil containing less than 2000 μg g^{-1} Pb. Lead levels in effluent from treatment ponds ranged from 25 to 21,400 μg L^{-1}, and effluent flow rate ranged from 1000 to 3500 m^3 d^{-1} during the operating life of the mine (1979-81). The stream flow ranged from extremes of 0.8-31 m^3 g^{-1}, and lead levels were about 5 µg L^{-1} upstream of the mine; downstream, the levels in one survey fell from 140 µg L^{-1} in the cove to less than 20 µg L^{-1} at the mouth of the cove. Sediment lead levels declined rapidly downstream to levels of 50-260 µg g^{-1}. The river has a low alkalinity (1-7 mg L^{-1} as $CaCO_3$) and is slightly acidic (pH 6.3-7.0), factors which should enhance lead accumulation.

In 1982, fish were captured 0.5 and 18 km downstream of the contaminated cove (Westlake et al., 1982). Near the mine, geometric mean blood lead levels ranged from 220 to 996 µg L^{-1}, with individual values ranging from 5 to 5100 µg L^{-1}. The most contaminated species were white sucker (Catostomus commersoni) and lake whitefish (Coregonus clupeaformis), while the least contaminated were white perch (Roccus americanus) and brook trout. Downstream, mean blood lead levels ranged from 45 to 69 µg L^{-1}, with the highest individual level of 680 µg L^{-1} in a white sucker. These blood lead levels indicate that toxicity to fish may have been occurring.

The activity of ALA-D was not inhibited in the expected pattern. There was some inhibition of activity in white suckers at both sites relative to what is considered 'normal' (Hodson et al., 1983), but the activities of other fish appeared unaffected. This anomaly may have been related to the presence of zinc in the river, although levels of zinc in fish tissues were not measured. A second alternative was that sample storage and handling affected the results, since the location was remote and samples sat for 1-3 d before analysis. A preliminary benthos survey indicated a depauperate invertebrate community in the cove receiving the mine discharge (Westlake and Smith, 1981).

Despite a very short operating life, highly localized contamination and attempts at minimizing the discharge of particulate lead, it is clear that lead impacts had occurred. Similar effects are likely in the Miramichi system in New Brunswick, where juvenile Atlantic salmon (Salmo salar) are heavily contaminated with lead from mining activities (Ray, 1978). In both cases, however, lead effects may be difficult to separate from those of zinc and copper pollution.

Great Lakes

The Great Lakes are not affected to any extent by lead mining. Nevertheless, the use of lead in gasoline and industry has enriched sediments, particularly in the lower lakes (Erie and Ontario), the site of most industrial and urban development. Hodson et al. (1984a) reported lead residues for a variety of biota from Lake Ontario, a lake demonstrating considerable enrichment of deep-water sediments (>150 $\mu g\ g^{-1}$ dry weight) relative to those in shallow water (<50 $\mu g\ g^{-1}$). Total waterborne lead levels are generally <1 $\mu g\ L^{-1}$, but inshore levels may be somewhat higher, particularly in harbours; reliable data are not available. The watershed of the east end of the lake is primarily agricultural or forested, while the west end is surrounded by city.

The data on lead in biota show consistent trends: levels are uniformly higher in the west end than the east, and concentrations decrease in the order plankton > zooplankton > inshore predatory fish > offshore planktivorous fish > offshore predatory fish. Lead in aquatic biota clearly reflected the east-west distribution of lead sources, the importance of proximity to lead sources and a negative food-chain biomagnification.

Offshore predatory fish (lake trout, Salvelinus namaycush) always contained less than 0.1 $\mu g\ g^{-1}$ total lead on a whole-body basis. While this indicates that complexation/precipitation reactions and dilution protect offshore fish, there is still a geographic trend in lead levels. In a survey of blood lead levels and erythrocyte ALA-D activities of Lake Ontario fish, Hodson et al. (1983) demonstrated an east-west increase in blood lead levels, although the mean levels were all less than 100 μg L^{-1}. Laboratory studies have demonstrated that whole-body analyses primarily reflect muscle lead of fish. Since lead does not accumulate to a high level in muscle, tissues such as blood, bone, liver and kidney provide a more accurate indication of lead exposure. The same survey also demonstrated that benthic species accumulated more lead than did fish feeding in the water column, reinforcing the observations on fish affected by mining.

In only one case in this survey did mean blood lead levels exceed 300 μg L^{-1}: white sucker from the St. Lawrence River at Maitland, Ontario. A subsequent study of fish at this site demonstrated mean blood lead levels for sucker of 694 μg L^{-1} and for carp (Cyprinus carpio) of 4864 μg L^{-1}; individual levels were as high as 17,100 μg L^{-1} in carp. The level of ALA-D inhibition, however, was only 40-45% of the expected inhibition, based on the observed lead levels and the response of laboratory fish. Subsequent analyses demonstrated that the lead contamination in this case was in the form of various alkyllead compounds (Chau et al., 1984), presumably from a local chemical plant manufacturing alkyllead.

Surveys of the Maitland site in 1981-84 (Hodson et al., 1984b) demonstrated the following:

1) Alkyllead compounds could be measured in effluent (160 μg L^{-1}), water (100-350 ng L^{-1}), sediment (0.27-0.7 mg kg^{-1} wet weight), macrophytes (ND-2.09 mg kg^{-1}), benthos (ND-0.33 mg kg^{-1}) and 13 species of whole or gutted fish (ND-3.5 mg kg^{-1}).

2) The spectra of di-, tri- and tetraalkyllead compounds in fish cor-

responded most closely to the spectra in water and effluent, and not to that in sediments. The most common forms in fish were tri- and tetraalkyllead.

3) The highest levels of contamination in fish were in 1981 (0.22-8.68 mg kg^{-1}), after which they declined and remained constant over the next 3 years (ND-3.5 mg kg^{-1}).

4) The most contaminated fish appeared to be yellow perch, sucker, carp and brown bullheads (*Ictalurus nebulosus*). The least contaminated were pike (*Esox lucius*) and centrarchids.

5) Total lead levels in the edible portion (muscle) were not closely correlated to levels in whole fish or gutted fish. Total alkyllead levels in muscle correlated well with total alkyllead in whole fish or gutted carcass.

6) There was a clear upstream/downstream distribution of residues when mean levels were compared. High levels in fish tissue (0.13-0.70 mg kg^{-1}) were observable at the furthest sampling site, 16 km downstream. Some contaminated fish were found upstream due to fish migration.

7) Alkyllead represented 0-100% of total lead, depending upon the location and species sampled. However, most fish in the contaminated area contained 50-75% of total lead as alkyllead.

8) There was no evidence of biomagnification in the local food-chain.

These observations indicate that alkyllead compounds are highly bioavailable. In laboratory studies, alkyllead was taken up and lost rapidly by rainbow trout (Wong et al., 1981); the loss may represent dealkylation rather than true excretion.

The effects of alkyllead contamination on aquatic biota at Maitland have not been investigated thoroughly. An earlier survey of benthic invertebrates downstream of the discharge of alkyllead indicated significant reductions in biomass and numbers of species (Griffiths, 1978). Of 10 fish sampled in 1982 and examined for histopathology, the 2 most highly contaminated exhibited some nerve and muscle damage. Furthermore, a population of northern pike downstream of the source, known as 'Johnstown pike', has a high prevalence of spinal curvatures (personal communication, Dr. J. Casselman, Ontario Ministry of Natural Resources), a symptom of lead-induced neuropathy. Since many other contaminants and some parasitic infections can induce a similar problem, studies are needed to show conclusive links.

A second potential effect is that of toxicity to human consumers of fish. The levels of total alkylleads in the edible portion of fish in 1983 ranged from 0.06 to 3.48 $\mu g\ g^{-1}$, the latter value being for yellow perch (Perca flavescens), a local sports species. There are currently no guidelines to protect human health from alkyllead compounds in fish, and few or no data on the oral toxicity of alkyllead compounds. Nevertheless, the 1984 'Guide to Eating the Sports Fishes of Ontario' (OME and OMNR, 1984) contains a warning about excessive consumption of fish in the Maitland area.

Conclusions

This review has demonstrated that lead entering aquatic ecosystems is readily taken up by aquatic biota from water and sediments. This exposure causes important toxic effects that are observable at levels of lead exposure typical of surface waters near known sources of lead in Canada and around the world. No case study was thorough enough to link lead exposure to lead residues in tissues of aquatic biota, these residues to biochemical and physiological effects and these effects to major changes in ecosystem structure and function. However, there are enough parts of the complete chain to recognize important detrimental effects of existing contamination of aquatic ecosystems.

These may range from lost productivity when organisms are eliminated from a stream, to lost utility when fish are no longer fit for human consumption. These effects occur in Canada and are most acute near lead mines and alkyllead manufacturing plants. Lead contamination from urban development is less severe, but cannot be ignored, since it is associated with a multitude of other toxic chemicals.

Research Needs

1) If Canada continues to use alkyllead compounds in gasoline, further research is needed on movement, cycling, residence times, sinks and effects in aquatic ecosystems. Of particular importance are the issues of the health of humans and aquatic biota and the technology needed to eliminate the discharge of alkyllead compounds.

2) The links between lead effects on individual organisms (laboratory and field observations), lead levels and important ecological effects have not been described quantitatively. Research is needed to link these measurements as a basis for pollution control and to enable a rapid diagnosis of ecological effects from simple measurements of response and contamination of individual organisms.

3) The complexation and precipitation of lead in natural waters have generally been regarded as beneficial processes of detoxification. However, enhanced lead contamination and toxicity to benthic organisms indicate that the problems may have simply been transferred from the water column to the sediments. Research is needed on factors that control the mobility, bioavailability and effects of sediment lead.

4) Existing lead contamination of aquatic ecosystems may ultimately disappear as sources dry up and sediments are covered up. However, the

environmental costs of waiting until that time must be balanced against the cost of immediate clean-up. Research is needed on the rate at which existing contamination from different sources will be reduced through dilution, burial in sediments and chemical immobilization.

Summary

1) The concentrations of total waterborne lead that are toxic to aquatic biota range from about 4 to 500,000 $\mu g\ L^{-1}$.

2) The most important causes of this variation include:

- water quality--organic and inorganic complexation
- the form of lead--Pb(II) versus Pb(IV)
- species sensitivity
- the age of the exposed organism.

3) Lead is readily accumulated by aquatic biota from water; accumulation from diet and sediments is less certain. Bioconcentration factors (the ratio of tissue to waterborne concentrations) decrease from 20,000 in algae to less than 1000 in fish. Field studies confirm that lead concentrations are not biomagnified in food-chains.

4) Symptoms of lead exposure include lead accumulation, enzyme inhibition, anemia and deformities in fish, reduced rates of growth, reproduction and survival of invertebrates and fish, and reduced productivity of all biota.

5) Field studies of lead pollution in England, Sweden, the United States, Nova Scotia and the Great Lakes demonstrate that:

- lead concentrations in edible portions of fish are often higher than the recommended limit for human health
- enzyme inhibition and other physiological changes typical of laboratory toxicity tests are readily observed

- populations of algae, benthos and fish may be reduced or completely eliminated, depending upon the severity of contamination
- benthic fish species are more contaminated with lead than pelagic species.

6) Alkyllead compounds released during their manufacture are 10-20 times more toxic and 10 times more concentrated in biota than inorganic lead.

7) Of several research needs, the most important is the evaluation of the fate and effects of alkyllead compounds, particularly their entry into human food.

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10. TERRESTRIAL BIOLOGICAL MONITORING OF LEAD USING LOWER PLANTS

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Introduction

The atmosphere plays an important role in terms of the pathways, cycles and transformations of lead in the Canadian environment. The atmosphere is significant for the transport and dispersion of lead, and the subsequent deposition from the atmosphere is influential in determining lead exposure conditions. Biomonitors have been used extensively to describe the end result of these transport, dispersion and deposition processes. The physical, chemical and biological properties of bryophytes and lichens facilitate their use as monitors of lead deposition from the atmosphere. The all-encompassing objective of monitoring is to determine spatial and/or temporal trends in levels and/or effects of lead, including lead that, relative to its source(s), is deposited or transported locally, regionally, nationally or continentally. The scope of this paper will be to outline the use of bryophytes and lichens in support of the above objective.

Criteria for Suitable Biomonitors

Monitors can be identified on the basis that they (i) have the provision for regular surveillance, and (ii) quantify how much pollutant is present (Martin and Coughtrey, 1982). The implication of monitoring is that changes over a period of time can be studied, and that comparisons in both time and amount will be possible. In addition, quantification should enable spatial comparisons to be made and the variation in the amount of pollutant within a given geographical area to be described. Martin and Coughtrey (1982) outlined the characteristics of suitable biomonitors.

Bryophytes and lichens have characteristics which meet several requirements of the ideal biological monitor for monitoring deposition. These include the following:

1) Some species have large geographical ranges (e.g. circumboreal), allowing comparison of metal concentrations from diverse regions, and such species can be found in urban, industrial and rural areas.

2) Morphology of bryophytes and lichens does not vary with seasons, thus accumulation can occur throughout the year; also, these plants are perennial, which has led to their use as long-term integrators of atmospheric deposition.

3) These plants have morphological features which enhance metal uptake, notably the absence of a well-developed cuticle, minimizing any physical resistance to the diffusion of soluble minerals into the plant interior.

4) These plants have the ability to accumulate metals to levels far greater than their expected physiological needs. This characteristic is explained, in part, by the ion-exchange properties of these plants; also, the plant surface, structure and roughness facilitate the interception and retention of atmospheric particulates.

5) Finally, the applicability for monitoring atmospheric deposition is emphasized in that bryophytes and lichens, unlike higher plants, do not have a well-developed root structure, and are thus dependent for their mineral nutrients on material deposited through wet and dry deposition to the plant surface.

Comparison of the Biological and Physical Measurements of Lead Deposition

The acceptability of using lichens and mosses to monitor atmospheric metal concentrations and deposition rests, in part, on how well the information provided by these plants corresponds to information obtained by traditional physical and chemical methods. The relationship between measured atmospheric metal concentrations and in situ lichen-moss metal concentrations has not been rigorously examined, but parallelism has been observed between the geometric and arithmetic means of metal concentrations in atmospheric particulates and lichens in the urban area of Sendai, Japan (Saeki et al., 1977). A general indication that lichens reflect atmospheric deposition was the observed tendency for element concentrations in lichens to remain in a narrow range, even though substrates varied in their element composition, indicating some other factor was influencing lichen element composition. Jenkins and Davies (1966) suggested that this factor would have to be regional in nature, and suggested atmospheric particulates based on a comparison of metal levels in lichens and dust-fall.

Comparisons of metal levels in cryptogams and precipitation have shown similar empirical relationships. Linear correlations between copper, lead and zinc concentrations in in situ *Brachythecium rutabulum* and bulk precipitation have been described by Andersen et al. (1978), while linear relationships were inferred between annual deposition estimates (in precipitation) and metal concentrations in *Hylocomium splendens* (Hanssen et al., 1980; see also Thomas et al., 1983). In a more mechanistic study, metal levels in transplanted *Hypogymnia physodes* and *Dicranoweisia cirrata* and bulk precipitation were compared on a monthly basis (Pilegaard et al., 1979). Metal levels in bulk precipitation followed a decreasing power curve relationship when the distance from the source was increased, and metal levels in transplanted lichens and mosses and *in situ* lichens showed the same response.

Comparisons have been made of the actual deposition rates described by biological and physical monitoring methods. Groet (1976) used biomass of and metal concentrations in *Leucobryum glaucum* to calculate metal deposition rates for the north-eastern United States. For lead, one estimate gave a rate of 23.8 mg m^{-2} a^{-1} for northern New Hampshire, which agreed quite well with the value of 19.6 mg m^{-2} a^{-1} reported by Schlesinger et al. (1974) on the basis of bulk precipitation samples. However, the cadmium deposition rate was much greater than estimates made using the moss concentrations. Similarly, deposition estimates based on concentrations in mosses and other bulk precipitation studies (Lazrus et al., 1970) agreed for nickel but were widely divergent for copper and zinc. The annual productivity of *Sphagnum* was used by Pakarinen and Tolonen (1976) to estimate lead deposition rates (2.8 mg m^{-2} a^{-1}) in central Finland, which corresponded to deposition rates (3.5 mg m^{-2} a^{-1}) measured by precipitation monitoring. Glooschenko and De Benedetti (1983) also conclude that deposition rates calculated from moss concentrations were of the same order of magnitude as those calculated from precipitation data. Further, Pakarinen (1981c) combined *Sphagnum* productivity and concentration data to estimate deposition rates for different parts of Europe. Lead deposition ranged from 2.1 mg m^{-2} a^{-1} (Finland) to 42 mg m^{-2} a^{-1} (England/Denmark) (see also Ruhling and Tyler, 1971; Furr et al., 1979; Lotschert and Wandtner, 1982).

Source Identification of Metals Accumulated by Cryptogams

A question of key interest is often the source of lead accumulated by lower plants. There are several approaches to identifying sources of the accumulated metals. The plant metal content will be influenced by natural and anthropogenic sources. Natural sources include the marine aerosol, leachates from foliage and bark and suspended particulates derived from local and remote soils and bedrock. The most widely used method for identifying sources is the gradient method, where metal levels are seen to increase with increasing proximity to the suspected source. Examples include the identification of the marine aerosol as a major chloride source for lichens by virtue of declining chloride levels with increasing distance from the sea (Brown and Di Meo, 1972).

Similarly, a distinct relationship was seen between lichen metal content and distance from the smelting complex in Sudbury, Ontario (Nieboer et al., 1972; Tomassini et al., 1976), with increasing lichen metal levels being observed as a function of increasing proximity to the complex (see also LeBlanc et al., 1974; Hocking et al., 1978). Lead emissions from vehicles have been identified as a source based on declining lead levels in lichens and mosses with increasing distance from roadsides (Ruhling and Tyler, 1968; Takala and Olkkonen, 1981).

Gough and Erdman (1977) used linear regression to evaluate the relationship between metal levels in Parmelia chlorochroa and distance from a coal-fired power plant in Wyoming, USA. Negative regression lines were drawn for many elements, indicating that the lichen metal concentrations decreased with increasing distance from the plant. The regression lines were significantly different from zero for 13 of the 29 elements examined. Six elements showed relatively large coefficients of determination, and a large coefficient of determination was considered good evidence that a point-source effect was being demonstrated. In this example, lead levels in lichens were not linked to the coal-fired power plant.

When several sources are potential contributors, the question of source identification and the relative contribution from each source becomes complex. In this situation, source identification has been made on the basis of (i) comparing plant element levels with those of the potential source and (ii) the relationships existing between element levels within the plant.

The comparison of plant metal concentrations with potential sources has been approached by calculating enrichment factors. Enrichment factor calculations have been extensively used to identify natural and anthropogenic sources contributing to the atmospheric aerosol (Chen and Duce, 1983; Lannefors et al., 1983). Puckett and Finegan (1980) calculated enrichment factors for 20 elements in 14 lichen species collected from 45 sites in the Northwest Territories, Canada. The potential source used in the comparison was crustal rock, and the resulting ratio was normalized by an element considered to be the most unambiguous indicator of the source material. The general formula described below was used to calculate the enrichment factor (EF):

Enrichment factor for any element (X) in the
lichen relative to crustal rock

$$= \frac{(X/\text{reference element})\ \text{in lichen}}{(X/\text{reference element})\ \text{in crustal rock}}$$

Scandium was used as the reference element, and the average levels of elements in crustal rock were used in the calculation. Enrichment factors near unity imply that the element was non-enriched with respect to average crustal rock, and hence strongly indicate that crust-derived material was the source of those non-enriched elements. Similarly, elements with EF values much greater than unity were considered to be enriched, and suggested the presence of sources other than crust-derived material. The elements aluminium, chromium, iron, sodium, titanium and vanadium had mean EF values of 1-5 for all species. These low EF values indicated that, relative to average values for crustal rock, there was no enrichment of these elements in the lichens concerned (Puckett and Finegan, 1980). For other elements (chlorine, lead and sulphur), consistently higher EF values were obtained. These higher values for lead were interpreted in terms of sources of lead, both natural and anthropogenic, in addition to crustal-derived material.

Several attempts at source identification have been based on relationships existing between element levels within the plant. For example, high correlations between sulphur and vanadium in Hypogymnia physodes (Laaksovirta and Olkkonen, 1977, 1979) were thought to represent a contribution to the lichen metal content from the combustion of fossil fuel. High intercorrelations between metal concentrations in lichens and mosses have been interpreted to indicate common or specific sources for the metals in several studies (Ellison et al., 1976; Garty et al., 1977; Furr et al., 1979; Boileau et al., 1982). In addition, multivariate statistical techniques have been effectively used to identify sources contributing to the atmospheric aerosol (Neustadter et al., 1976; Gaarenstroom et al., 1977; Parekh and Husain, 1981; Chen and Duce, 1983). These techniques have recently been applied to identify element sources for bryophytes and lichens.

Puckett and Finegan (1980) used ordination techniques, and the resulting element associations were examined in relation to sources external to the plant. Principal component analysis (PCA) was carried out on the data from three species, Cetraria cucullata, C. nivalis and Cladina stellaris, collected in the Northwest Territories. In all cases, the first five components explained 81-89% of the variation in the element concentrations. These components were considered in the context of lichen enrichment from crust-derived particulates, the marine aerosol and certain anthropogenic sources. Both *C. cucullata* and *C. nivalis* had components which were highly weighted for lead, and these components were judged to be representative of emissions from the combustion of leaded gasoline.

In contrast, the components identified by Saeki et al. (1977) from the analysis of the element content of *Parmelia* spp. were mainly anthropogenic in origin. Component one had high weightings for iron, chromium, aluminium and copper, and represented soil-derived material; the second component was weighted strongly for mercury and lead, and was interpreted as being derived from residential heating emissions and vehicle emissions. Component three was variable in its weightings, differing in each lichen examined.

In another Canadian study, *Cladina rangiferina* was collected from sites near Saint John, New Brunswick (Puckett and Finegan, 1981), and the lichen element concentrations were analysed by PCA. The first three components accounted for 93% of the total variation in the seven elements studied. Component one was designated the 'dust' or 'earth' factor, as it corresponded to high weightings for iron, titanium and chromium. Component two, with high weightings for sulphur, vanadium and nickel, was interpreted as an 'industrial' factor characterized by emissions from combustion of fossil fuels. Component three had a high weighting for lead, and was attributed to inputs from automobile exhaust. Identification of components was based, in part, on the enrichment factors calculated for the metals.

Garty et al. (1977) used discriminant analysis to differentiate between different settlements on the basis of the metal content of the lichen Caloplaca aurantia. Nickel and zinc were found to be the most suitable metals for the distinction between settlements of differing size. A comparison of correlation coefficients between metals accumulated by C. aurantia in differing settlements showed differences from which metal sources were inferred, based on agricultural and industrial activities.

Another approach to source identification is based on the varying isotopic composition of some elements, which depends on the origin and treatment of the parent material. In this approach, the isotopic ratios of certain elements in the potential source and in the plant are determined. Case (1980) examined sulphur isotope abundance in lichens collected around a sour-gas processing plant in Alberta, Canada. The lichen sulphur content generally increased as the gas plants were approached, and with increasing proximity the lichen sulphur isotopic composition gradually changed and approached the isotopic ratio of the emitted SO_2. Similarly, Jaakkola et al. (1983) attempted to calculate the relative contributions from different lead sources to the lichen lead burden by determining the ratios of stable lead isotopes in lichens and potential lead sources such as gasoline and incinerator ash.

Spatial and Temporal Distribution of Lead and Other Metals

Biomonitoring using lichens and bryophytes has been undertaken to examine both spatial and temporal aspects of metal deposition. Spatial studies fall into three main categories based on source characteristics:

- line-source emissions
- point-source emissions
- remote sources.

Line Source Emissions

Increased concern over the dispersion and subsequent effects of lead emitted by the use of leaded gasoline in automobiles had resulted in numerous studies of lead accumulation in plants in roadside environments (Martin and Coughtrey, 1982).

Transects from roadsides in southern Sweden showed that *Pleurozium schreberi* had accumulated lead concentrations as high as 500 μg g^{-1} at the roadside (Ruhling and Tyler, 1968), and concentrations declined with increasing distance from the roadside. Similarly, Takala and Olkkonen (1981) found that lead concentrations in the lichen *Hypogymnia physodes* decreased as a function of distance up to 100 m from the road, and that the lead levels in the lichen reflected differing traffic densities, allowing zones to be described corresponding to high and medium traffic densities within the urban area of Kuopio, Finland. In contrast, Laaksovirta et al. (1976), using *Hypogymnia physodes* in Kuopio, noted decreasing lead concentrations with increasing distance from the roadside, but found no correlation between lead content of the lichen and traffic density (see Takala and Olkkonen, 1976; Moore et al., 1978; Lawrey and Hale, 1981).

Point-source Emissions

Bryophytes and lichens have been used to describe distribution around a variety of point sources of atmospheric metal emissions (Table 1), ranging from peat-fired power plants (Folkeson, 1981), chlor-alkali plants (Wallin, 1976), pulp and paper mills (Barclay-Estrup and Rinne, 1979), nickel smelters (Nieboer et al., 1972) to steelworks (Pilegaard, 1978).

Burkitt et al. (1972) used *Eurhynchium* and *Parmelia* species to study cadmium, lead and zinc distributions near a smelting complex in the United

Kingdom, and noted the general decline in metal levels in the plants with increasing distance from the complex. This general decline, common to most investigations around point sources, can be expressed mathematically, allowing for a quantitative estimate of any change in the distribution pattern as the result of changes in emissions.

Atmospheric dispersion models have been used extensively to estimate regional air concentrations and deposition of metals around point sources. Initial attempts with the combined use of biological indicators (higher plants) and dispersion models in air pollution monitoring are described by Jokinen et al. (1982). Lichens and mosses have not been used to a large extent in testing/verifying these models. Nash and Sommerfeld (1981), in their study around coal-fired power plants in New Mexico, USA, found the highest metal concentrations in lichens adjacent to the plant. Based on a Gaussian plume model, maximum particulate deposition should occur 2-6 km from the stack, and the distance predicted corresponded very closely to the position of sites with the highest lichen element concentrations. Another example of linking dispersion models and element levels in cryptogams is the study by Ratcliffe (1975), in which moss lead levels were compared with predicted atmospheric lead concentrations.

In addition to describing distribution patterns, moss/lichen metal levels can be used to estimate what proportion of a certain emission is deposited locally. Lead concentrations in bryophytes and other vegetation were used to show that only a minor portion of the lead dispersed from roadsides was deposited within 50 m of the roadside (Ruhling and Tyler, 1969). A similar approach has been used to estimate the local deposition of mercury around a chlor-alkali plant (Wallin, 1976).

Table 1.

Studies around point-source emissions using lichens and mosses.

Emission Source	Species		Elements	Author
Iron and steel plants	*Hypnum cupressiforme*	(B)*	Cd, Cu, Fe, Mg, Mn, Pb, Zn	Ellison et al. 1976
	Lecanora conizaeoides	(L)*	Ca, Cd, Cr, Cu, Fe,	Pilegaard 1978
	Cladonia furcata	(L)	Co, Cr, Cu, Fe, Mn,	Goyal & Seaward 1981
	Coelocaulon aculeatum	(L)	Ni, Pb, Zn	
	Peltigera membranacea	(L)		
	P. rufescens	(L)		
Power plants				
coal-fired	*Parmelia chlorochroa*	(L)	35	Gough & Erdman 1977
peat-fired	*Pleurozium schreberi*	(B)	Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	Folkeson 1981
Smelters				
(a) Copper	*Hylocomium splendens*	(B)	As, Cd, Cu, F, S,	LeBlanc et al. 1974
	Pleurozium schreberi	(B)	Pb, Zn	
(b) Lead/Zinc	*Eurhynchium paraelongum*	(B)	Cd, Pb, Zn	Burkitt et al. 1972
	Parmelia spp.	(L)		
(c) Nickel	9 lichen species		Cu, Fe, Mn, Ni, Pb, Zn	Nieboer et al. 1972
	Corticolous lichens		Cu, Ni	Hocking & Blauel 1977
Uranium mining	*Cladonia rangiferina*	(L)	Pb, U	Beckett et al. 1982
	C. mitis	(L)		
	Pleurozium schreberi	(B)		
	Sphagnum spp.	(B)		

* (B) = bryophyte; (L) = lichen.

Table 2.

Regional studies of element distribution using bryophytes and lichens.

Location	Species	Elements	Reference
EUROPE			
	Lichens		
Finland	*Cladonia arbuscula*	Ca, Cu, Fe, K, Mg, Mn, N, P, Pb, Zn	Pakarinen 1981a
Finland	*Cladonia arbuscula* *C. mitis*	Cu, Fe, Mn, Pb, Zn	Pakarinen et al. 1978
Denmark	*Hypogymnia physodes* *Lecanora conizaeoides*	Cd, Cr, Cu, Ni, Pb, V, Zn	Pilegaard et al. 1979
	Bryophytes		
Sweden	*Hylocomium splendens* *Hypnum cupressiforme* *Pleurozium schreberi*	Pb	Ruhling and Tyler 1968
Sweden	*Hypnum cupressiforme*	Cu, Cr, Ni, Pb, Zn	Ruhling and Tyler 1969
Sweden	*Hypnum cupressiforme*	Ca, Cr, Ni, Pb, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn	Ruhling and Tyler 1971
Sweden	*Hylocomium splendens* *Pleurozium schreberi*	Cd, Cu, Ni, Pb, V, Zn	Ruhling and Skarby 1979
Sweden, Norway, Finland	*Hylocomium splendens*	Cd, Cr, Cu, Fe, Ni, Pb, Zn	Ruhling and Tyler 1973
Norway	*Hylocomium splendens*	28	Steinnes 1977
Finland	*Sphagnum fuscum*	Cd, Cr, Cu, Fe, Hg, Mn, No, Ni, Pb, Zn	Pakarinen and Tolonen 1976
Finland	*Sphagnum fuscum*	Ca, Cu, Fe, K, Mg, Mn, No, Ni, Pb, Zn	Pakarinen 1981a
Finland, Norway, USSR, W. German, Great Britain	*Sphagnum* spp.	Ca, Cu, Fe, Mg, Mn, Pb, Zn	Pakarinen 1981a

Table 2. (Cont'd)

Sweden, Denmark	*Hylocomium splendens*	As, Cd, Co, Cr, Cu Mo, Ni, Pb, V, Zn	Gydesen et al. 1983
Denmark	*Hypnum cupressiforme*	Cd, Cr, Cu, Ni, Pb, V, Zn	Pilegaard et al. 1979
Poland	*Hylocomium splendens*	Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn	Grodzinska 1978
W. Germany	*Hypnum cupressiforme*	Be, Cd, Cu, Ni, Pb, Zn	Herrmann 1976
W. Germany	*Sphagnum magellanicum* *S. rubellum* *Polytrichum strictum*	Cd, Cu, Mn, Pb, Zn	Lotschert and Wandtner 1982
W. Germany, Holland	*Hypnum cupressiforme*	Pb	Thomas 1979
NORTH AMERICA			
	Lichens		
Eastern Canada	*Cladina rangiferina*	Pb, S	Zakshek et al. 1985
	Bryophytes		
New England, US	*Leucobryum glaucum*	Cd, Cr, Cu, Ni, Pb, Zn	Groet 1976
New York State	11 *Sphagnum* species	35	Furr et al. 1979
Maritime Provinces	*Sphagnum magellanicum*	Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, S, Zn	Percy 1982

Remote Sources

Bryophytes and lichens have also been used to describe regional gradients in lead deposition (Table 2). Regional transport and deposition have been studied by sampling three common woodland mosses (*Hylocomium splendens*, *Pleurozium schreberi* and *Hypnum cupressiforme*) collected in areas remote from roads, large population centres and industrial plants in southern-central Sweden (Ruhling and Tyler, 1968). A distinct north-east - south-west gradient was revealed for all three species, with a doubling of lead concentrations seen in the south-west compared with the north-east. The lead content could be related, in part, to precipitation amount. Nevertheless, the observed gradient in lead concentrations was considerably greater than the corresponding precipitation gradient; the moss lead concentrations still exhibited a clear gradient after standardization for precipitation.

Comparison of Hylocomium splendens collected from the most northern and southern regions of Sweden showed that cadmium and lead concentrations were fivefold higher in the south, whereas two- to threefold differences were noted for cobalt, copper, chromium, iron, nickel and zinc. In contrast, the calcium, magnesium, manganese and potassium levels either were only slightly different or showed no differences between the regions. These initial surveys were extended to examine the distribution of other metals in southern Sweden using Hypnum cupressiforme (Ruhling and Tyler 1969, 1971).

In a more localized survey (100-km transect), copper, chromium, lead, nickel and zinc concentrations were again significantly lower in the north-east (Ruhling and Tyler, 1968). In a further north-east - south-west transect (300 km) at higher latitudes, lower copper, lead and nickel concentrations in Hypnum cupressiforme were found in the northeastern region. Normalization of the metal concentrations for precipitation amounts did not remove the gradient for copper or lead, but concentration differences for other elements were equalized on the basis of the normalization. Contribution from the marine aerosol was discounted as being the major factor responsible for the observed gradients, as were regional differences in bedrock weathering rate and regional differences in the productivity and decomposition of moss carpets. The authors concluded that the observed gradients were the result of higher metal deposition (of anthropogenic origin) in southern Sweden than in northern Sweden.

A more intensive survey of Sweden involving 1000 sites at which Hylocomium splendens, Pleurozium schreberi and Hypnum cupressiforme were collected corroborated the regional distributions described earlier, and also served to describe locally high concentrations around mining and smelting regions (Ruhling and Skarby, 1979). Ruhling and Tyler (1973) extended their survey using Hylocomium splendens to include Finland and Norway. Metal concentrations were usually highest in southern and south-western regions of Finland and Norway, with the lowest concentration in northern regions. For several metals--cadmium, chromium and nickel--sources internal to the countries were more important than external sources in influencing deposition patterns. Lead concentrations were considered to be enhanced by sources external to the countries surveyed. This conclusion was made on the basis of comparisons between lead emissions and lead deposition (as measured by moss; Ruhling and Tyler, 1971) as well as the similarity between lead deposition (in moss) and sulphur deposition (in precipitation) patterns in southern Scandinavia. In southern Sweden, almost 50% of the deposited sulphur is considered to originate from foreign sources.

Steinnes (1977, 1980) extended the observations of Ruhling and Tyler (1973) in southern Norway to include the whole country. Twenty-eight elements were examined in collections of Hylocomium splendens, and distinct distribution patterns were observed for several groups of elements. Confirmation that cadmium and lead concentrations were highest in southern Norway was obtained, and several other metals, notably antimony, chromium and vanadium, showed a similar pattern. Because there were no major sources of these metals in southern Norway, Steinnes concluded that sources outside Norway were responsible for the observed pattern. The results from the moss analyses were substantiated by a parallel air and precipitation monitoring exercise (Hanssen et al., 1980) and soil analyses (Allen and Steinnes, 1980).

Pilegaard et al. (1979) used the same species (Hypnum cupressiforme) as Ruhling and Tyler to describe the deposition patterns of seven elements in Denmark. Regional differences were again found, with the highest concentrations in eastern and south-eastern parts of the country. However, Pilegaard et al. (1979) concluded that this continuity implied that local industrial emissions in the Danish-Swedish border regions had been underestimated, and that contributions from the long-range transport from other areas had been overemphasized. The authors further concluded that the data from southern Sweden and Denmark were best explained in terms of local pollution originating from both Denmark and Sweden being superimposed on a more widespread regional pattern caused by the long-range transport of material from sources south of Scandinavia.

Herrmann (1976) also used epiphytic Hypnum cupressiforme to describe the spatial distribution of metals throughout the Federal Republic of Germany. Of the metals examined, cadmium, copper, lead and zinc were highly intercorrelated. Regional differences were apparent, with the highest moss metal concentrations occurring in the industrial regions of the Rhine and the Ruhr and the northern Hartz mountains, and the lowest concentrations being found in lower Bavaria and parts of northern Germany.

Thomas (1979) collected epiphytic Hypnum cupressiforme from 37 sites along a transect through Middle Europe extending from the Alps in southeastern West Germany to the Netherlands coast. The transect passed through varied land use types, including forests and agricultural, urban and rural areas. The lead concentration of the moss reflected industrial activities along the transect, with the highest concentrations being found at points where either heavy industry was located (the Ruhr area) or high automobile traffic density was apparent. Grodzinska (1978), using Hylocomium splendens and Pleurozium schreberi, found regional differences in Poland, and classified the regions into relatively clean, moderately contaminated and heavily contaminated on the basis of nine metal levels including lead. In general, the lowest metal concentrations were found in mosses from national parks in northern Poland and the highest in southern Poland, a distribution corresponding to the pattern of industrial emissions in Poland.

In the studies quoted, distribution patterns were described mainly using the woodland mosses Hylocomium splendens and Hypnum cupressiforme; while showing distinct regional patterns, the interpretations may be confounded by substrate influences on the moss metal concentrations. Such canopy influences can be removed by the use of moss/lichens found on ombrotrophic peat bogs which receive their nutrients from wet and dry deposition directly to the bog surface. Consequently, Sphagnum and Cladonia species, the dominant moss/lichen generally found on ombrotrophic bogs, have been used extensively to describe regional deposition patterns in Scandinavia and North America. Pakarinen and Tolonen (1976) used Sphagnum fuscum to describe the deposition of 10 elements throughout Finland. In agreement with the earlier observations using Hylocomium splendens, highest cadmium and lead concentrations were found in southern Finland. Also, Lotschert and Wandtner (1982), using Sphagnum magellanicum, S. rubellum and Polytrichum strictum, found distinct regional differences in the distribution of cadmium, copper, lead, manganese and zinc in West Germany.

Lichens, colonizing ombrotrophic peat bogs and mineral soils, have been used to describe regional deposition patterns in Fennoscandinavia. Pakarinen (1981a, b) showed that Cladonia species from ombrotrophic bogs had significantly higher copper, iron, lead, sulphur and zinc concentrations in southern Finland than in the central or northern parts of the country. A similar pattern was observed for the same species collected from mineral soils (Pakarinen et al., 1978), and in both studies the higher lichen metal concentrations in the southern region of Finland were attributed to regional smelting and refining activities. Other factors, such as growth rate and metal-retaining capacity, were considered not to exhibit regional characteristics that would significantly counteract the influence of metal deposition from the atmosphere. The similarities between the regional distribution as seen by Ruhling and Tyler (1973) using the woodland moss Hylocomium splendens, Pakarinen and Tolonen (1976) using Sphagnum fuscum and the patterns described by Cladonia spp. indicate that similar regional gradients can be observed using different bryophytes and lichens, and that the regional gradients are probably not related to substrate characteristics (see also Pakarinen, 1981a).

In North America, regional studies are limited in number. Groet (1976) analysed mosses from north-eastern United States and found wide regional differences. Chromium, copper, lead and nickel concentrations were generally highest in the southern, more industrialized portion of New England. The average concentrations of metals, with the exception of zinc, were considerably higher than the levels found in remote areas of Canada, suggesting that high levels of airborne metals were present in the New England region. The influence of urban centres on the regional deposition pattern was recognized, with deposition from the local sources being superimposed on the regional pattern. Regression analyses using New York City as a representative major source showed a significant decrease in metal levels with increasing distance from the city. In addition to New York City, emissions from additional sources at greater distances were suggested to contribute to moss metal concentrations, but no supporting data were described. Furr et al. (1979) collected mostly Sphagnum spp. from the Adirondack region of New York State, upwind of major urban centres, and analysed the plant material for 46 elements. Lead levels were higher than suggested baseline values (Bowen, 1966) and, although lead mines operate in the Adirondacks, the high intercorrelation between lead, mercury, selenium and antimony was interpreted as representing contributions from the long-range transport of these metals.

In Canada, a regional survey of metal and sulphur concentrations in the lichen Cladina rangiferina showed that lead and sulphur concentrations in eastern Canada consistently exceeded those found in the Northwest Territories (Zakshek et al., 1985). At all sites, lead concentrations in the lichen exceeded those found in the Northwest Territories by a factor of 2, and at some sites a 10-fold difference was approached (Figure 1). Lead and sulphur emissions in eastern Canada are much higher than in the Northwest Territories, and the differences in lichen sulphur and lead concentrations between the two regions are a quantitative reflection of these differences in emissions. This regional survey was extended to see if regional gradients in sulphur and lead concentrations existed within eastern Canada. In summary, regional gradients in lead concentrations (Figure 2) were not as well defined as those for

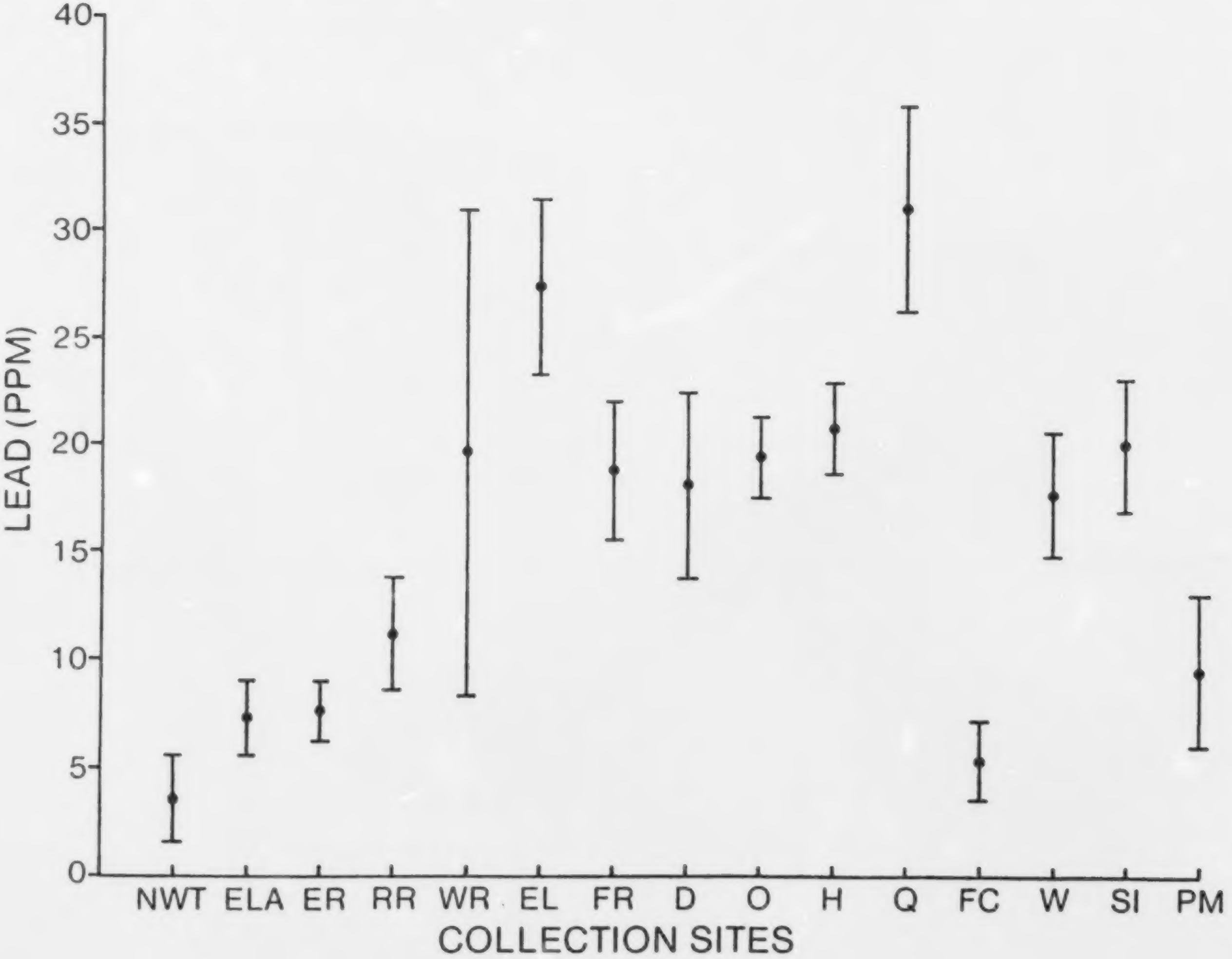

Figure 1. Lead Concentrations in C. rangiferina from Eastern Canada and the Northwest Territories.

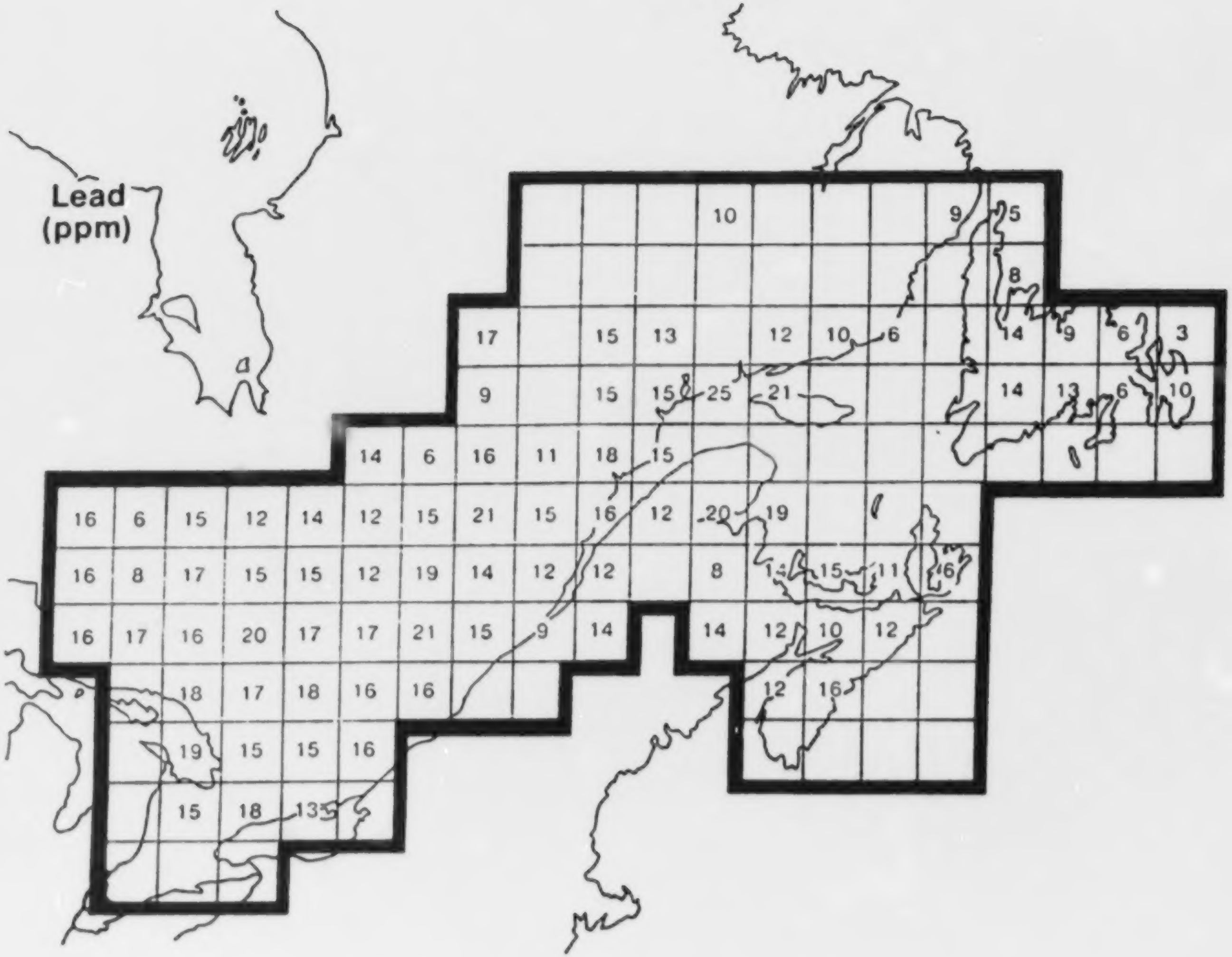
Lead
(ppm)
10 9 5
8
17 15 13 12 10 6 14 9 6 3
9 15 15 25 21 14 13 6 10
14 6 16 11 18 15
16 6 15 12 14 12 15 21 15 16 12 20 19
16 8 17 15 15 12 19 14 12 12 8 14 15 11 6
16 17 16 20 17 17 21 15 9 14 14 12 10 12
18 17 18 16 16 12 16
19 15 15 16
15 18 13

Figure 2. Lead Concentrations in *C. rangiferina* in Eastern Canada.

The figure in each grid square is the mean value of five replicate samples of *C. rangiferina* taken from a single ombrotrophic peat bog in that grid square.

sulphur. Higher lead values were found throughout the study area in contrast to the pattern for sulphur, where the highest concentrations were localized in central Ontario and southern Quebec. In general, higher lead concentrations (15-20 μg g^{-1}) were found throughout southern Ontario and southern Quebec, with the lowest concentrations (< 10 μg g^{-1}) in the more remote areas (Newfoundland).

Percy (1982) examined the metal content of *Sphagnum magellanicum* from 61 sites in the Maritime Provinces of Canada. There was no regional-scale pattern in element concentrations in either an east-west or north-south direction. Most elements, including lead, showed a uniform concentration across the region, with localized regions of enrichment attributable to adjacent point or area sources.

Temporal Studies

Changes in metal deposition over long time scales have been described by analysing herbarium material collected as early as the mid-19th century. This results in a qualitative assessment of historical metal levels, and allows for a comparison with present-day conditions. Ruhling and Tyler (1968) examined herbarium material of three woodland mosses collected in southern Sweden over the period 1860-1968 to determine whether changes in moss lead levels had occurred over that period. Four distinct changes in lead concentrations were observed. Initially, lead levels approached 20 μg g^{-1} for the period 1860-75. The concentration doubled between 1875 and 1900, but then remained at 40-50 μg g^{-1} until 1950. Concentrations rose steeply to 80-90 μg g^{-1} in the period after 1950. The first increase was interpreted as showing the rise in industrial emissions possibly associated with increased coal-burning during 1875-1900, and the second increase was explained in terms of the large increase in the combustion of leaded gasoline after 1950. In other retrospective studies, levels of nine elements were determined in the epiphyte Pterogonium gracile collected in 10 different years during the period 1944-76 in a rural area in Denmark (Johnsen and Rasmussen, 1977). Significant increases were observed in the lead, vanadium and zinc contents; increasing trends were seen for chromium, copper and nickel, but cadmium showed no such tendency. Confidence in the described trends is increased by the fact that the same tree was sampled in all 10 collection times. The increasing lead, vanadium and zinc levels were linked to increasing anthropogenic emissions of the metals, and the concentrations in the plant were calculated to double in 20, 60 and 110 years, respectively. Similarly, Rasmussen (1978) sampled five bryophytes of the same trees in 1951 and 1975, and showed that levels of cadmium, copper, iron, lead, nickel, vanadium and zinc had increased between 42 and 108%.

In North America, Rao et al. (1977) quoted unpublished data of Robitaille and LeBlanc on the cadmium, chromium, copper, nickel, lead and zinc levels in herbarium material of five mosses collected from Mont Royal, Montreal, between 1905 and 1971. When the average concentrations in the mosses were compared over the years, the authors concluded that most metal concentrations were increasing, indicating steadily increasing metal deposition in the area, through growing urbanization and industrialization. Increasing lead levels in lichens from the north-eastern United States have been demonstrated (Lawrey and Hale, 1981) by examining the lead concentrations in three lichen species collected over the period 1907-79. Lead levels increased 20-fold over the period, but the higher lead levels had occurred only relatively recently (post-1965).

However, there are indications that lead levels are declining in some areas. Pakarinen (1981c) found that iron, lead and zinc concentrations in *Sphagnum* spp. had declined considerably from the mid-1970s to 1980, indicating that atmospheric deposition has decreased significantly (Table 3). Pakarinen linked the lower moss metal concentrations to several factors, such as the reduced lead content in gasoline, more efficient emission controls on industrial sources and a general decline in industrial activity over the period studied. Ruhling and Skarby (1979) compared moss metal concentrations in collections between 1968 and 1970 with those in collections in 1975. The cadmium, copper and lead concentrations in Sweden were largely identical, but localized high concentrations of nickel and zinc had disappeared, interpreted

Table 3.

Changes in the metal concentrations of the surface moss layer (*Sphagnum fuscum*, 0.3 cm) between 1975-76 and 1979-80 (from Pakarinen, 1981c).

Site Number	Location	Sampling Date	Concentration ($\mu g\ g^{-1}$) Fe	Mn	Zn	Pb
8	Klaukkalansuo	20.10.76	699	92	38.8	30.8
	"	9.10.76	392	46	28.0	20.9
	"	4.5.80	347	155	28.8	18.8
	"	23.7.80	359	220	25.6	16.9
	"	4.10.80	306	137	24.11	13.6
9	Munasuo	9.6.76	567	185	33.1	20.2
	"	17.5.80	220	323	24.9	8.9
10	Kananiemensuo	22.10.76	649	74	37.1	21.4
	"	12.10.80	290	214	23.1	15.2
14	Torronsuo	1.10.75	570	268	49.4	33.7
	"	18.10.80	226	473	23.1	10.5
20	Kaurastensuo	11.10.76	303	229	27.1	15.0
	"	2.8.78	333	124	22.8	15.3
	"	14.9.80	230	194	22.3	10.2
Mean % change between 1975-76 and 1980			48%	75%	-34%	-48%

to be the result of local emission control measures. A similar comparison in 1980 showed significant declines (Gydesen et al., 1983). Cadmium, chromium, nickel, lead, vanadium and zinc concentrations in mosses declined by 30-40% in most of southern and central Sweden during the 5-year period from 1975 to 1980 (Table 4). The only area with rising levels was found on the north-east coast of Sweden in the vicinity of a mining/smelting complex. The reasons given for this decline were similar to those described above by Pakarinen (1981c).

Summary

Bryophytes and lichens have been used to assess air quality for over a century, and recently their use as biomonitors of deposition from the

Table 4.

The average concentrations (μg g^{-1}) in various parts of Sweden of heavy metals in moss in 1975 and 1980 (from Gydesen et al., 1983).*

Location	Year	As	Cd	Cu	Cr	Ni	Pb	V	Zn
SW Sweden	1975	0.33	0.81	9.1	3.9	3.5	62	7.2	83
	1980	0.32	0.56	8.7	2.3	2.4	37	4.8	59
SE Sweden	1975	0.29	0.74	7.7	1.9	3.3	48	5.8	70
	1980	0.28	0.55	7.6	1.5	2.1	29	4.4	56
W central Sweden	1975	0.20	0.67	6.8	2.7	3.4	45	5.0	67
	1980	0.24	0.43	7.1	2.1	2.5	27	3.9	54
E central Sweden	1975	0.27	0.62	8.7	10.8	6.5	42	5.9	74
	1980	0.24	0.49	7.8	3.7	3.3	28	5.0	57
NW Sweden	1975	0.20	0.39	5.4	0.9	2.1	17	1.4	47
	1980	0.16	0.29	4.5	0.7	1.5	11	1.5	47
NE Sweden	1975	0.55	0.64	10.0	1.5	2.5	33	3.4	59
	1980	0.81	0.48	13.5	2.9	2.0	32	3.9	63

* Each value is based on analyses of about 50-100 moss samples. The concentration levels in E central Sweden and NE Sweden are in some cases influenced by local enhancements caused by emissions from metal industries.

atmosphere has been given considerable attention. This contribution addresses the criteria for suitable biomonitors for lead deposition, and to what extent bryophytes and lichens satisfy these criteria. The comparability of biological and physical measurements of lead deposition is considered, as is the question of the source identification of the lead accumulated by cryptogamic plants. Examples of the use of biomonitors to describe the spatial and temporal variation in lead levels in response to differing lead sources are outlined.

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11. LEAD CONTAMINATION OF THE TERRESTRIAL ENVIRONMENT FROM LONG RANGE ATMOSPHERIC TRANSPORT

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Introduction

Most of the literature concerned with lead pollution of the environment deals with conditions in the vicinity of sources such as highways and smelters. Less emphasis has been placed on the impact on environments distant from sources or source regions of lead, in spite of the fact that atmospheric transport of this element on a global scale was demonstrated more than 15 years ago (Murozumi et al., 1969). In particular, the extensive lead contamination of soils in many remote areas has not been widely recognized.

Norway appears to be a suitable area for the study of long-range transport of pollutants, because the contribution from national sources to the atmospheric deposition of many pollutants is small compared with the amounts derived from sources out of Norway. The purpose of this paper is to review some recent work in Norway on the impact of atmospheric lead on the terrestrial environment. This work may be relevant to the situation in Canada because the two countries are similar in some ways. In both countries, a great part of the population is located within a relatively small area in the south-east, while most of the remaining areas are very sparsely populated. Both countries have arctic areas in the north with extensive areas of coniferous forests at more southerly latitudes, and both countries receive considerable input of long-range atmospheric pollutants from other countries to the south.

Lead in Air

Atmospheric lead concentrations were studied in detail at three stations in different parts of the country during 1978-79 (Hanssen et al., 1980). The highest levels were recorded at Birkenes in the south, with a mean concentration of 19 ng m^{-3}. The air concentrations of lead and other pollutants at Birkenes showed an episodic pattern. Most of the time, the lead level was below 15 ng m^{-3}. For short episodes, associated with transport from source areas in other parts of Europe as shown by air trajectory studies, levels as high as 100 ng m^{-3} were observed. Lead in air showed a strong positive correlation with elements such as Cd (R=0.90), V (0.88), As (0.88), Sb (0.91), Cr (0.80), Fe (0.79) and Mn (0.75). Calculated air trajectories were used to classify the air samples with respect to source regions by subdivision in eight sectors (Pacyna et al., 1984). By far the highest lead levels were observed with air from the south-west sector (mean value 48 ng m^{-3}).

Atmospheric Deposition of Lead

The atmospheric deposition of lead and a number of other elements was registered in 1977 using moss analysis (Steinnes, 1980). The results of this survey (Rambaek and Steinnes, 1980) showed that the lead deposition (Figure 1) is at a maximum in the southernmost part of the country, decreasing to about one-tenth of that level in areas of central and northern Norway which are less affected by long-range atmospheric transport. Other components such as 'excess SO_4', NO_3, Cd, V, As and Sb show similar geographic deposition patterns. The wet deposition of Pb, Zn and Cd has been monitored at four stations in different parts of the country since 1979. At Birkenes, in the south, the lead level is about 10 mg m^{-2} a^{-1}, and has remained relatively constant during this period. This value is similar to wet deposition levels of lead in

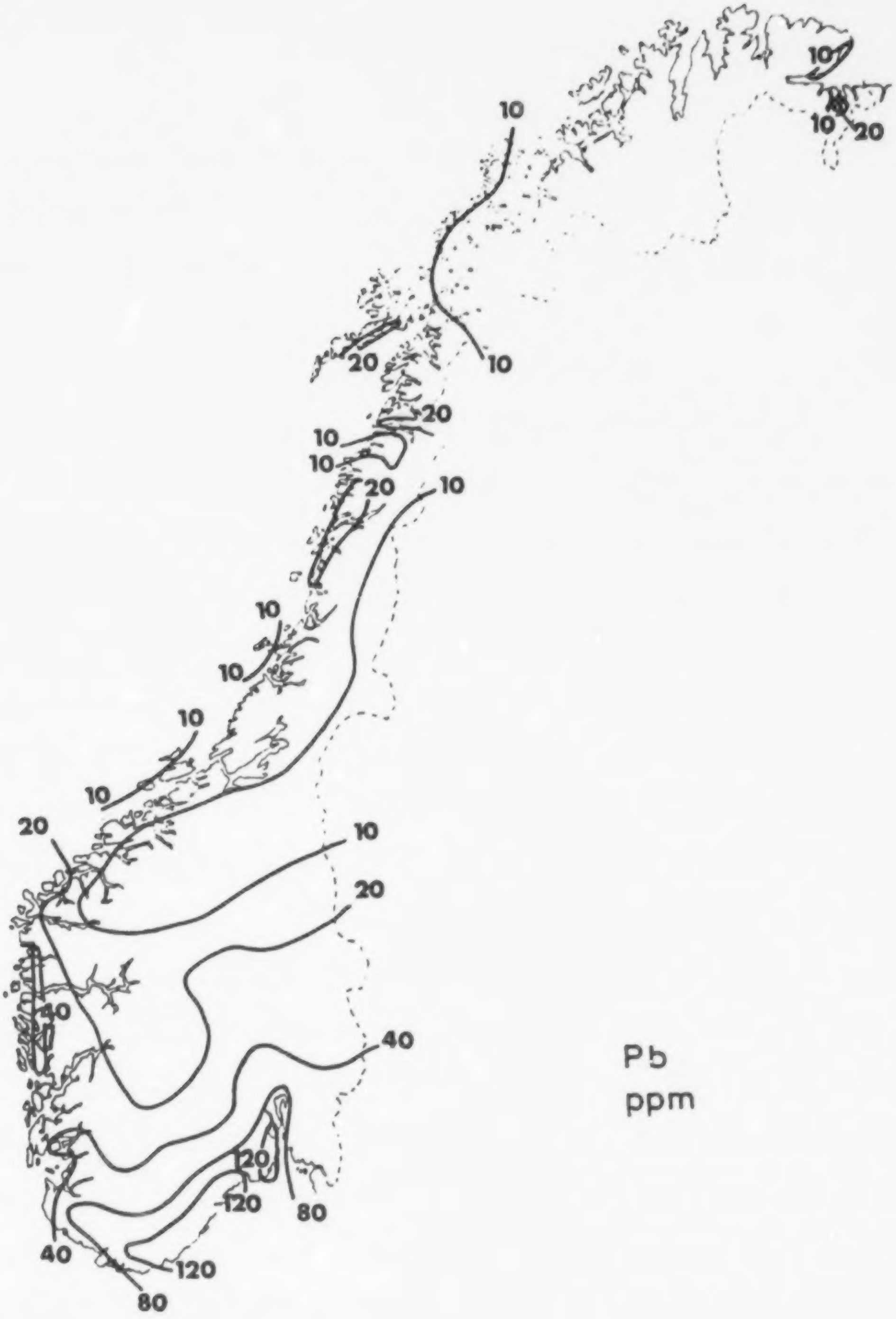
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Figure 1. Deposition Pattern of Lead in Norway as Evident from the Moss Survey 1977.

rural areas of West Germany (Nurnberg et al., 1982).

Lead in Natural Surface Soils

The geographical distribution of lead in natural, i.e. undisturbed and uncultivated, surface soils in Norway (Figure 2) is quite similar to that of the airborne deposition, indicating that lead in the surface soil is strongly dependent on atmospheric supply from long-range transport (Allen and Steinnes, 1980). In some local areas in southernmost Norway with high levels of orographic precipitation, the lead level in the humus layer exceeds 200 $\mu g\ g^{-1}$, whereas the corresponding figure for soils in the far north is less than 10 $\mu g\ g^{-1}$. Similar observations of high soil lead levels distant from major source regions have been reported from the north-eastern United States (Reiners et al., 1975; Siccama and Smith, 1978). Profile studies indicate that the excess lead in soils of southern Norway is confined to the A, and partly to the B, horizons, whereas the underground material does not appear to show any appreciable regional differences (Steinnes, 1984). Lead appears to be mainly associated with the soil organic matter. No similar data are available for lead in agricultural soils in Norway.

Cadmium shows a very similar geographical distribution in Norwegian natural soils to that of lead, indicating long-range transport as a major source also for this element. Whereas the Cd:Pb ratio in precipitation is about 1:50, the corresponding ratio in some of the very acidic soils of southern Norway is 1:100 or less, indicating that cadmium is less strongly fixed in the soil and thus more mobile in the terrestrial ecosystem. The higher mobility of cadmium in natural soils is confirmed by work reported from Sweden (Tyler, 1978, 1981).

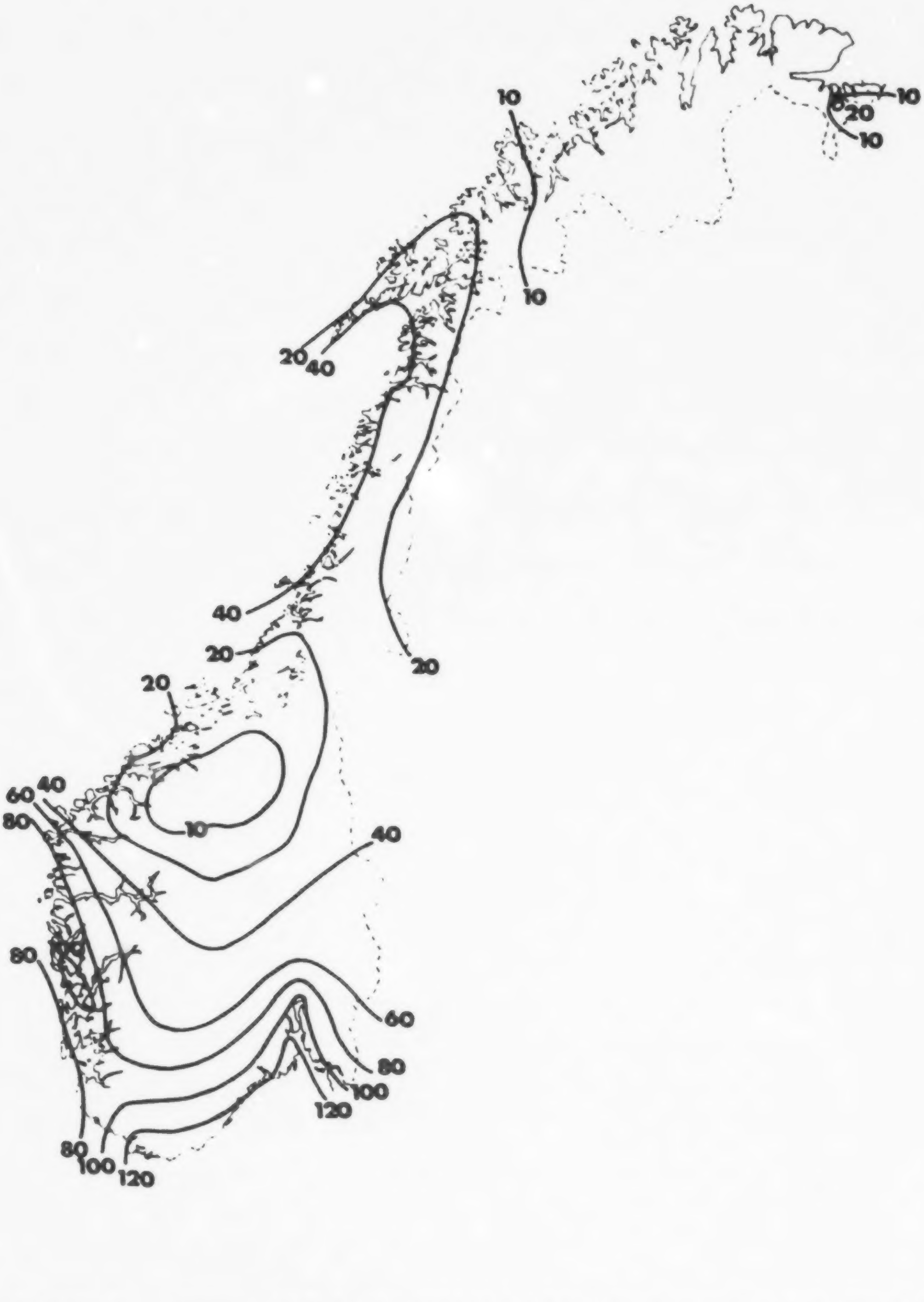
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Figure 2. Geographical Distribution of Lead in Norwegian Surface Soils.

Lead in Terrestrial Biota

Heavy metals supplied by long range atmospheric transport may be absorbed in plants through foliar deposition or via the soil through the root system. Pot experiments on arable land (Tjell et al., 1979) using a combination of radiotracer techniques and chemical analyses indicated that lead in rye-grass was mainly absorbed from the atmosphere, whereas cadmium was predominantly supplied through the root system. However, the soil cadmium may have been originally derived mainly from atmospheric deposition.

An investigation of major plant species from a number of coniferous forest localities in southern and central Norway, respectively (Solberg and Steinnes, 1983), revealed that lead and cadmium were present at about 5 times higher levels in southern Norway, corresponding fairly well with the differences in atmospheric deposition between the two regions. Some typical values are given in Table 1.

Table 1.

Lead and cadmium in vegetation from coniferous forest ecosystems in southern Norway (SN) and central Norway (CN).

		Pb ($\mu g\ g^{-1}$)		Cd ($\mu g\ g^{-1}$)	
Plant Species		SN	CN	SN	CN
*Hylocomium splendens**		65±21	5±1	0.55±0.18	0.07±0.02
Betula pubescens	Twigs	15±5	2.7±1.1	0.61±0.25	0.15±0.05
	Leaves	2.2±1.1	0.9±0.5	0.41±0.09	0.10±0.03
Pinus sylvestris	Twigs	15±4	2.0±0.7	0.96±0.31	0.10±0.04
	Leaves	3.4±1.3	0.6±0.2	0.37±0.17	0.02±0.01
Calluna vulgaris	Twigs	9.6±4.4	1.6±0.6	0.05±0.02	0.02±0.01
Vaccinium vitis-idaea	Twigs	5.0±1.8	1.3±0.6	0.14±0.06	0.02±0.01
	Leaves	1.5±0.7	0.3±0.1	0.02±0.01	-

* Reflecting *relative* atmospheric deposition between regions.

Studies of liver samples from lambs (Froslie et al., 1985) and cervides (Froslie et al., 1984) show that differences in atmospheric deposition levels also affect the uptake of lead and cadmium in ruminants. This pathway, however, does not seem to be important for the exposure of human beings.

Much work still needs to be done in order to further identify and quantify the pathways of lead--and other elements derived from long-range atmospheric transport--in terrestrial food-chains.

Historical Studies

Several authors have used lake sediments to reveal temporal trends in the atmospheric deposition of lead (e.g. Hanson et al., 1982; Evans and Dillon, 1982). Ombrotrophic peat bogs offer similar possibilities. In a study of peat cores from 20 ombrotrophic bogs in different parts of Norway (Hvatum et al., 1983), the vertical distribution profiles of lead and other elements were shown to exhibit large differences between different parts of Norway. Some typical data for lead are shown in Table 2. It appears that

Table 2.

Lead in peat profiles of ombrotrophic bogs in different parts of Norway.

Region	Locality	Pb (μg g^{-1}) 3-5 cm	10 cm	20 cm	50 cm
Southern Norway	As	145	100	17	5
	Idd	138	45	13	7
Western Norway	Askvoll	87	45	6	3
Central Norway	Smola	11	12	9	2
	Levanger	18	8	5	1
	Namsos	26	23	7	2
Northern Norway	Andoya	11	10	5	2
	Porsanger	7	5	2	1

even in the far north there is a distinct surface enrichment of lead. Since most plants do not absorb lead readily and thus would not contribute strongly to an active circulation of lead between the plant and the peat surface, the excess surface lead may be assumed to be derived from long-range transport even in this remote area.

Exposure of Man

In order to describe the pathways of lead in a terrestrial ecosystem (Wiersma, 1979) and from the environment to man, the use of compartment models seems to be convenient. These models require the establishment of 'transfer factors' between the various compartments. It is believed that the various data described in this paper could help to establish such factors.

The significance of long-range atmospheric transport to the lead exposure of human population groups is not very well established. Results from a recent Norwegian study, however, may indicate that the contribution from long-range transport is more important than assumed in the past. In that study (Sivertsen, 1985) involving the urban area of Sarpsborg/Fredrikstad with a population of 108,000, the contribution of long-range transport to the blood lead was calculated to be 26%.

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12. LEAD PATHWAYS THROUGH SOIL AND HOUSEHOLD DUSTS

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Introduction

Lead and many other heavy metals of present-day concern in terms of environmental pollution are present in rocks, soils, waters and air in small amounts from natural geological sources, which in turn may influence the chemical composition of potable water supplies, foodstuffs and the nature of airborne particles and dusts inhaled or ingested. Before attempting to assess the contribution of metal pollution to the environment, it is essential to obtain reliable baseline data on the natural amounts derived as a result of weathering processes on rock-forming minerals and subsequent geochemical cycling in the surface environment.

Soils developed in mineralized areas frequently contain high concentrations of one or more of the heavy metals lead, zinc, cadmium and copper. However, in Britain and in many other countries, much of the metal enrichment in soils is probably due to mining and smelting activities rather than the natural weathering of underlying material. In Britain, lead mining commenced in Roman and earlier times, thrived until the end of the 19th century and then declined rapidly. Peak output was in the mid-19th century when Britain produced around 50% of the world's lead. It has been estimated that over 4000 km^2 of land is now contaminated as a result of this mining activity (Davies, 1980; Thornton, 1980).

Present-day inputs of lead to the environment include both natural sources (e.g. volcanoes) and anthropogenic sources, including industrial emissions and effluents and vehicle exhaust fumes. Precipitation contains lead derived from all of these sources. Soils may also be contaminated as a result of fertilizer use and the addition of metal-rich sewage sludges and other organic waste materials. In urban areas, additional lead pollution may arise from the use of lead-containing paint and the local disposal of fossil fuel residues and other domestic wastes.

In the UK in 1981, some 9.7×10^3 t of lead were used in petrol (gasoline), of which 75% was released into the atmosphere (Chamberlain et al., 1978; Royal Commission on Environmental Pollution, 1983). This figure can be compared with estimated annual emissions from major UK lead industries of $0.2\text{-}0.25 \times 10^3$ t (Department of the Environment, 1974), from which it can be deduced that in general around 10% of lead in air is of industrial origin and the rest comes from vehicle emissions. Of course this ratio will vary between industrial, urban and rural environments, and could be reversed in the vicinity of major emitting sources such as a lead smelter.

World consumption of lead in fuel, together with estimated emissions, are shown in Table 1, and indicate considerable reduction over the past 5 years; data for some of the EEC member states for 1981 are shown in Table 2, although it must be stressed that these figures for lead consumption and emissions are based on the maximum permissible levels of lead and not the actual amounts used. For instance, while the maximum permitted level in Great Britain is currently $0.4\ g\ L^{-1}$ Pb, the actual amount for 1981 was $0.38\ g\ L^{-1}$ (Royal Commission on Environmental Pollution, 1983, quoting Petroleum Review). This accounts for the disparity between the calculated maximum lead consump-

Table 1.

World consumption of lead in petrol and estimated atmospheric emission from motor vehicles.

Year	Consumption* Pb (t)	Estimated Pb emission (t) (based on ca. 75% release)
1979	315,000	236,000
1980	260,000	195,000
1981	234,000	175,000
1982	238,000	178,000
1983	just over 200,000 (estimated)	150,000

* Data provided by Lead Development Association.

Table 2.

Petrol consumption, calculated maximum lead use and estimated maximum emission in some EEC member countries in 1981.

	Total Petrol Market* ($\times 10^6$ t)	Maximum Permitted Pb content (g L^{-1})	Calculated Maximum Pb Consumption (t)	Estimated Maximum Pb Emission (t)
United Kingdom	18.7	0.4	10,200	7,650
France	18.1	0.4	9,900	7,400
West Germany	22.3	0.4	4,600	3,450
Italy	12.0	0.4	6,600	4,950
Belgium	2.7	0.4	1,500	1,100

* Data published by Associated Octel Co. Ltd. (1983).

tion for Britain in Table 2 and the actual figure of 9.7×10^3 t quoted in the Royal Commission on Environmental Pollution's (1983) Ninth Report.

Around 10% of the lead emitted as inorganic lead aerosol from automobile exhaust is deposited on and within 100 m of roads (Little and Wiffen, 1978). In Britain it has been estimated that about 50% of the remainder of this lead emitted from automobiles is transported in the air and subsequently deposited within the country, and a similar quantity is exported elsewhere; this is shown diagrammatically in Figure 1 (Royal Commission on Environmental Pollution, 1983).

In Britain, long-term concentrations of lead in air for rural areas are usually below 0.15 $\mu g\ m^{-3}$, and in larger cities below 1 $\mu g\ m^{-3}$ (Royal Commission on Environmental Pollution, 1983); in the USA, concentrations in most rural sites fall below 0.2 $\mu g\ m^{-3}$, and most urban areas show an annual average lead concentration between 0.5 and 2 $\mu g\ m^{-3}$ (NAS, 1980). Air lead concentrations near main roads and motorways may be appreciably higher, ranging from 0.4 to 2.2 $\mu g\ m^{-3}$ near main roads in the London suburbs (Turner et al., 1980; mean values over a 3-month period in 1978) and from 6 to nearly 25 $\mu g\ m^{-3}$ in the central reservation of the M4 motorway (Colwill and Hickman, 1981; monthly mean values over the period 1973-79).

The annual lead deposition rate of some 20 mg $m^{-2}\ a^{-1}$ previously reported for rural areas in the UK can be greatly exceeded in urban areas where values up to 360 mg $m^{-2}\ a^{-1}$ have been found (Royal Commission on Environmental Pollution, 1983). In New York and Chicago, values of around 100 mg $m^{-2}\ a^{-1}$ have been quoted, although in rural food-growing areas of the mid-west and southern USA, values were less than 10 mg $m^{-2}\ a^{-1}$ (Lazrus et al., 1970). Rates of lead fall-out are discussed in greater detail by Chamberlain (1983).

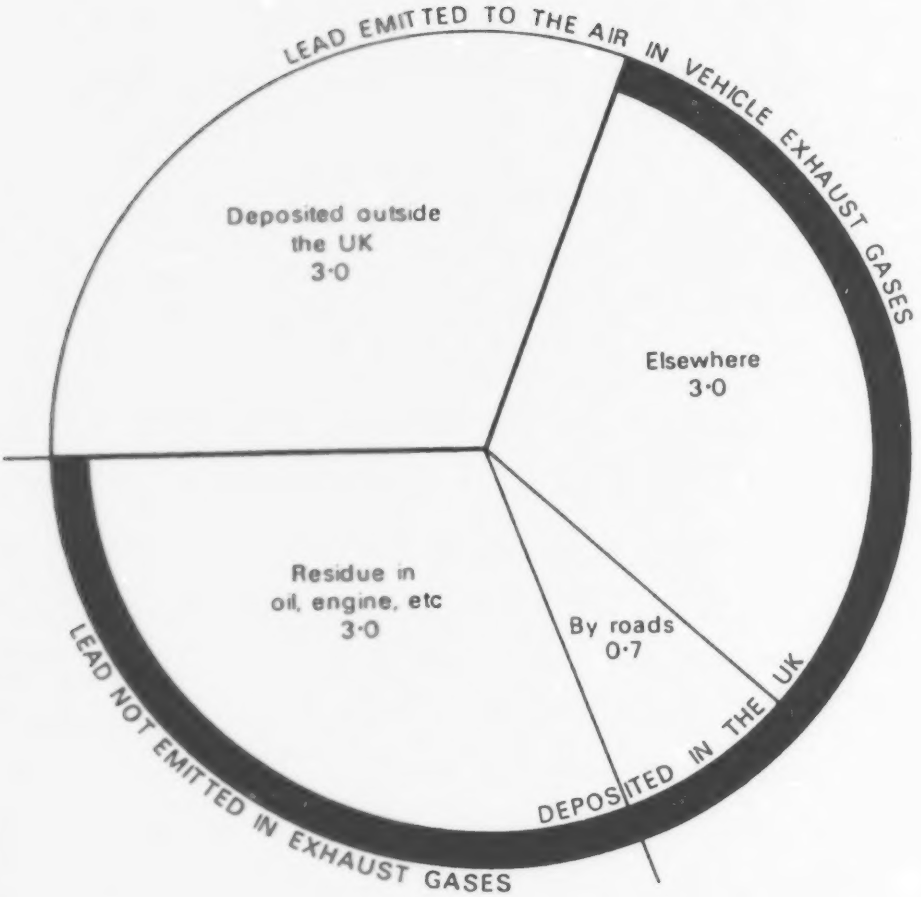

Figure 1. Fate of Lead Added to Petrol in the UK. Figures are in thousand tonnes per year and are approximations for 1981.

SOURCE: Royal Commission on Environmental Pollution, 1983.

He proposed that if 100 mg m^{-2} a^{-1} is taken as an upper limit for the present rate of deposition of exhaust lead in the UK, excluding zones of a few tens of metres alongside very busy roads, then the cumulative fall-out of exhaust lead in cities since 1946 is about 2 g m^{-2}.

Chamberlain et al. (1978) reviewed extensive investigations into lead aerosols in the environment undertaken by the United Kingdom Atomic Energy Authority at Harwell. An assessment of particle size concentration and dispersion of ambient lead aerosols at a variety of roadside sites indicated that lead emitted from cruising vehicles is mainly in the form of very small discrete particles of about 0.03 μm in diameter. However, in urban conditions, where vehicles accelerate strongly, and in car parks when the aerosol had aged, particles ranged from 0.2 to 2 μm in diameter, with some lead attached to conglomerate particles. Roadside concentrations are usually about 2 μg m^{-3} for each 1000 petrol-driven vehicles per hour. Again concentrations were found to decline rapidly with distance from the road: only about 10% of airborne lead emitted from vehicles is deposited within 100 m of the road. Calculations based on traffic flow and concentrations of airborne lead at various distances from a road suggest there is a zone of about 15 m wide on either side of a road where the concentration of lead exceeds 1 μg m^{-3} for every 1000 vehicles per hour (averaged over a 24-h period).

It is of interest that, as a result of a survey of 500 humus samples taken from uncultivated areas over the whole of Norway (avoiding populated areas and at distances exceeding 500 m from main roads and 250 m from local roads), concentrations of lead were found to be over 10 times as high in southernmost areas of the country than in areas in the far north (Allen and Steinnes, 1979; Steinnes, 1983). Mean values ranged from 0 μg g^{-1} in the north to 108 $\mu g\ g^{-1}$ in the south; the authors proposed long-range atmospheric transport of lead from sources in Europe to the south and south-west of Norway in the absence of any apparent geochemical differences.

Direct evidence for widespread regional contamination in Britain has been provided by Lee and Tallis (1973). From a study of peat profiles in remote areas, they recognized two major periods of pollution. The first resulted from rapid growth of industry during the 18th and 19th centuries, and the second from the great expansion of motor vehicle traffic since World War II.

Regional Geochemical Maps

The requirement for systematic data on heavy metal levels in the UK has been met in part by regional geochemical surveys carried out by the Applied Geochemistry Survey (previously known as the Institute of Geological Sciences). These surveys are based mainly on the systematic collection and analysis of stream sediment samples. Methods of compilation, etc., and the interpretation of the maps have been described by Thornton and Plant (1980). The map showing the distribution of lead over England and Wales is shown in Figure 2. This highlights the principal mineralized areas in England and Wales, and also reflects centres of present-day and recent lead smelting. A halo of elevated lead concentrations is shown around the city of Birmingham, Britain's second largest conurbation. The maps for zinc and cadmium show patterns of distribution similar to that of lead. Regional contamination of these metals is derived from the same principal sources. This serves to illustrate that contamination of the surface environment is frequently related to more than one metal.

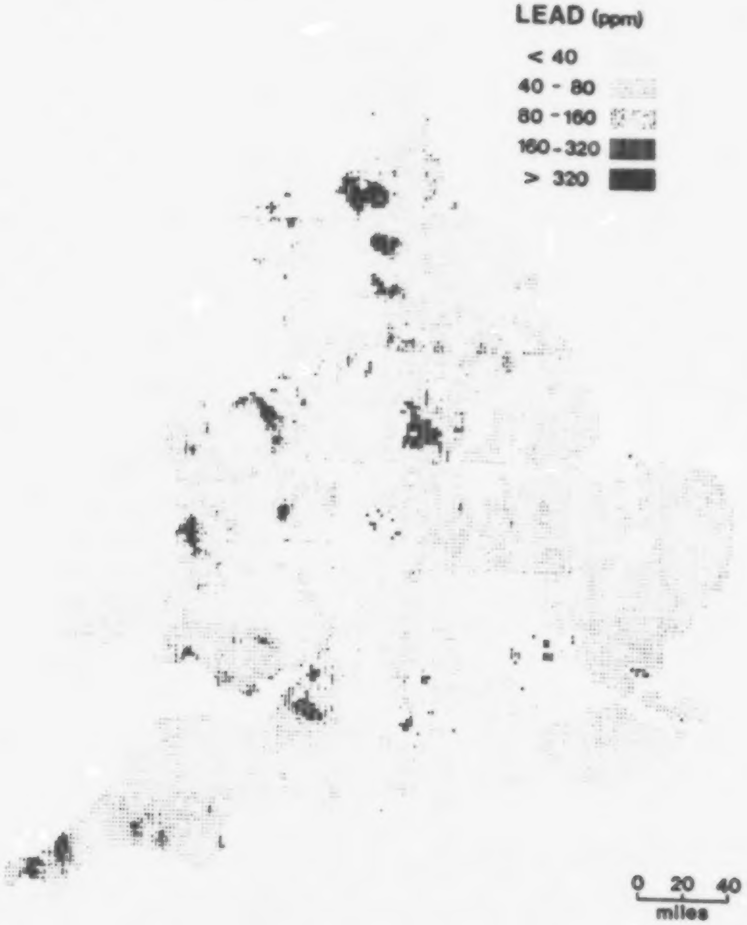
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Figure 2. Distribution of Lead (ppm) in Stream Sediments in England and Wales.

Maps of this kind provide valuable information on regional patterns of lead distribution, focussing attention on large areas of contamination and at the same time reflecting differences in the metal content of uncontaminated rocks and soil. They do not, however, show small-scale pollution on a field-by-field basis, or reflect localized contamination alongside major roads, etc.

Lead in Agricultural Soils

Surface soils (0-15 cm) sampled on 226 farms in England and Wales (Archer, 1980) showed a median lead concentration of 42 μg g^{-1} and a range of 5-1200 μg g^{-1}. A recent statistical survey of soil data from Britain (Davies, 1983) indicated that the normal surface soil (0-15 cm) lead content lies between 15 and 106 μg g^{-1}, with a geometric mean of 42 μg g^{-1}. Higher levels of lead usually arise as a result of anthropogenic activity. Reaves and Berrow (1984) examined the distribution of lead in 3944 samples from 896 Scottish soil profiles. The geometric mean content of all mineral samples was 13 μg g^{-1} Pb and of all organic samples 30 μg g^{-1} Pb. The mean lead content of 462 samples in the depth range 7.5-12.5 cm was 54 μg g^{-1} Pb compared with 15 μg g^{-1} Pb for the depth range 47.5-52.5 cm. Holmgren et al. (1983) reported values for 3001 surface soil (Ap) samples from cropland in the USA The median concentration was 11 μg g^{-1} Pb and the mean 18 μg g^{-1} Pb. It is of interest that soil lead concentrations in the USA appear lower than those in Britain. The relatively high values observed in British topsoils may indicate a widespread low-level contamination arising from some two centuries of industrial activity.

The Soil-Plant-Animal Relationship

Thornton (1983a, b) reviewed the subject of soil-plant-animal interactions in relation to disorders in grazing livestock, and drew attention to the importance of seasonal effects on the content of lead in the shoot material of pasture herbage. In a study of 11 farms in the old lead-zinc mining area of Derbyshire, England, with soils ranging from 95 to 5100 $\mu g\ g^{-1}$ Pb, the lead content of the herbage dry matter remained relatively low throughout the grazing season, but rose significantly in winter months, when the herbage was ungrazed and the plants in a senescent stage (Figure 3). A similar rise in the lead content of grass in winter had previously been noted in Britain (Mitchell and Reith, 1966), although the reasons were not clear. It is possible that several factors may contribute, including (i) an accumulation of lead from airborne sources on lead surfaces during the ungrazed winter months, (ii) redistribution of lead within the plant during senescence, and (iii) a change in the dry matter composition in the senescent plant material. Although there was little difference between the lead content of pasture during the cattle-grazing season on the 11 farms mentioned above, Thornton and Kinniburgh (1978) reported a broad relationship between bovine blood lead values and the lead content of the soils, ranging from around 10 $\mu g\ dL^{-1}$ blood on soils containing 100-400 $\mu g\ g^{-1}$ Pb to 30 $\mu g\ dL^{-1}$ blood on contaminated soils with 1000-2000 $\mu g\ g^{-1}$ Pb. Some of the results have been summarized in Figures 4 and 5, showing (i) the response in blood lead to increasing levels of lead in the soil, (ii) a much larger range in blood lead values in cattle on high-lead soils than on low-lead soils, and (iii) a positive relationship between blood lead and faecal lead, and faecal lead and soil lead (Thornton et al., 1986). It is emphasized that none of the cattle on the 11 farms showed any ill effects resulting from lead intake, nor did the high lead status of the Derbyshire environment lead to any obvious effect on animal production or health.

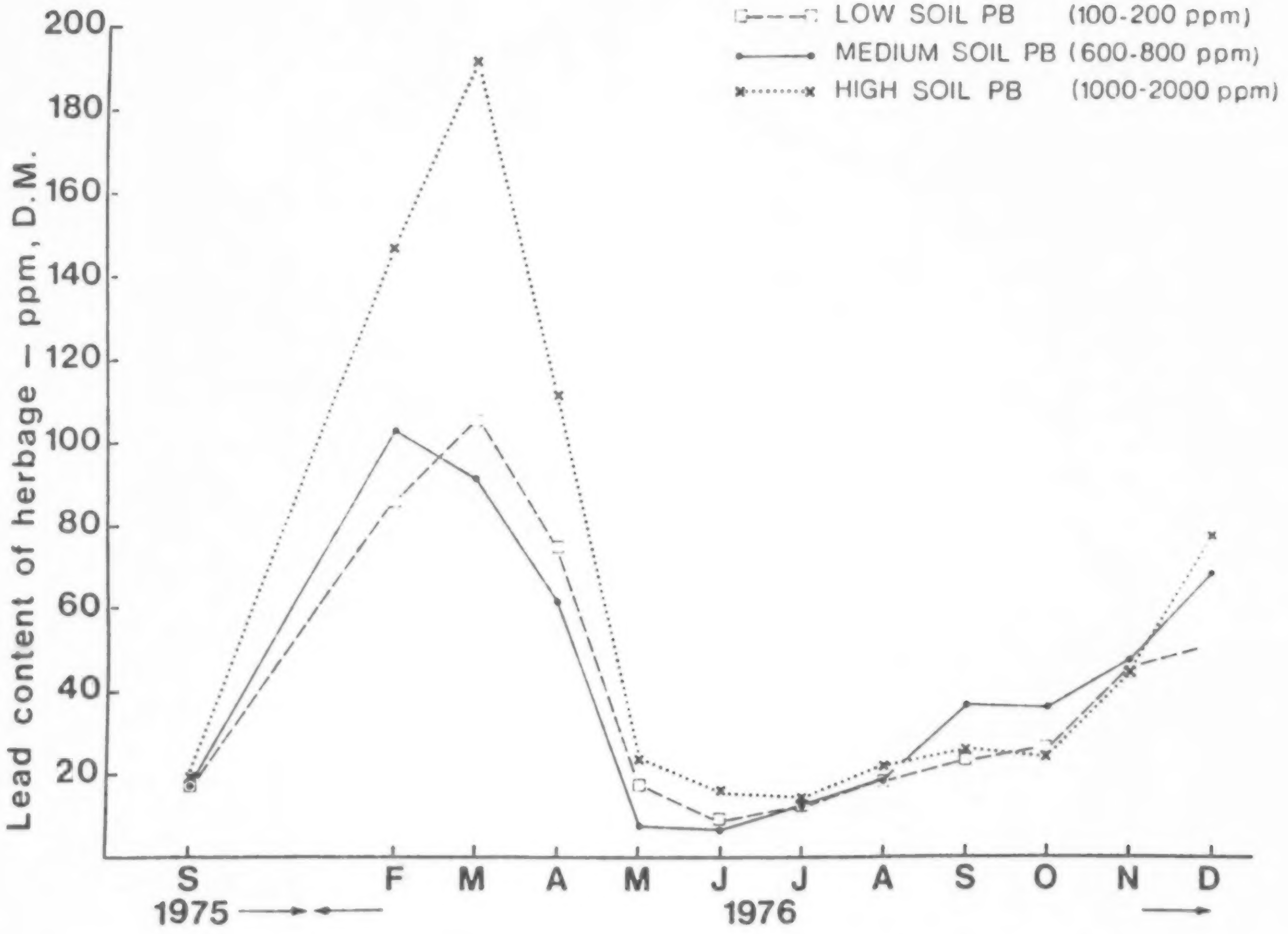

Figure 3. Seasonal Variations in the Lead Content of Mixed Pasture Herbage Growing in Soils of Varying Lead Status in Derbyshire, England.

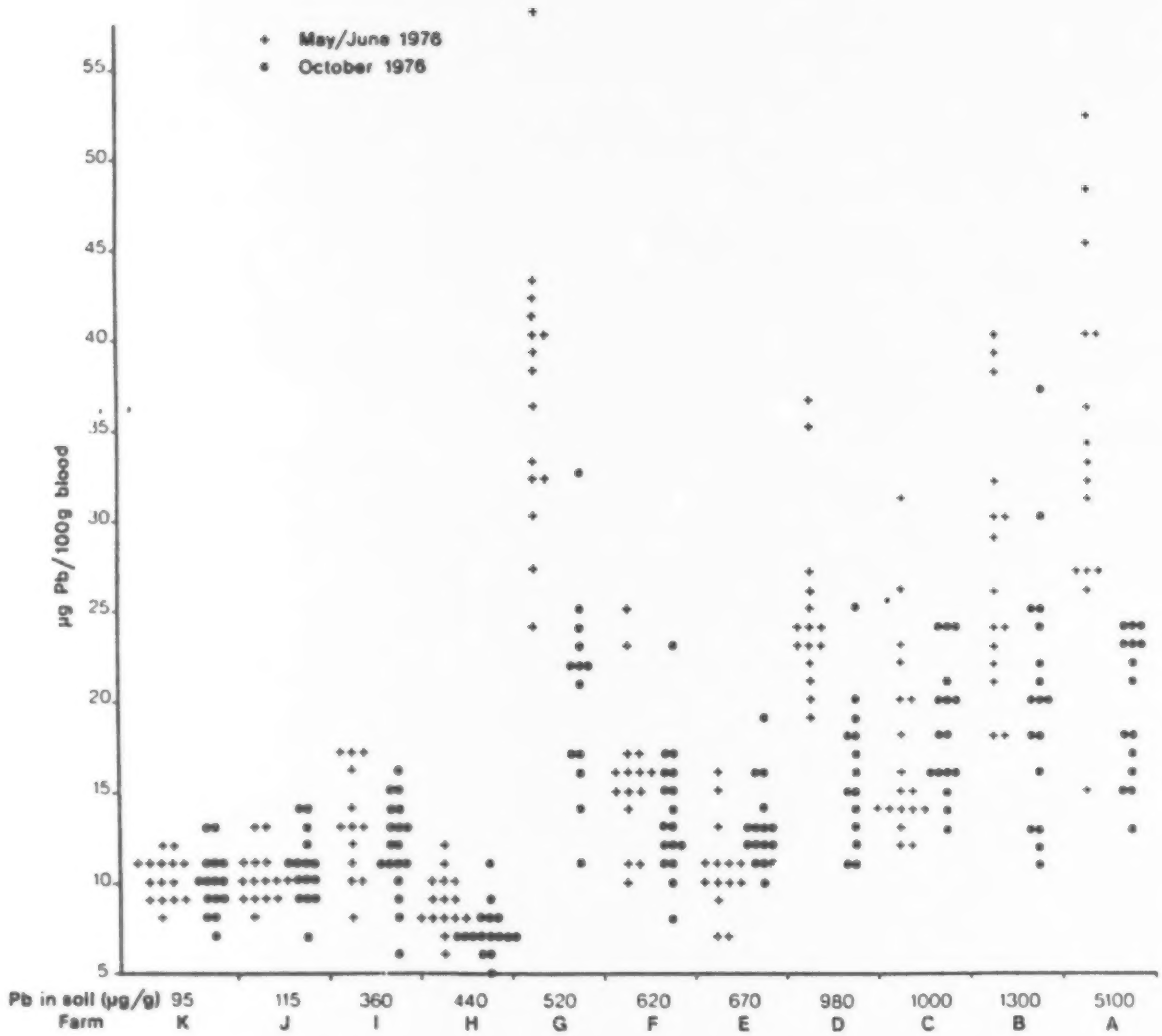

Figure 4. Blood Lead Values in Cattle Grazing Land of Varying Lead Status in Derbyshire, England.

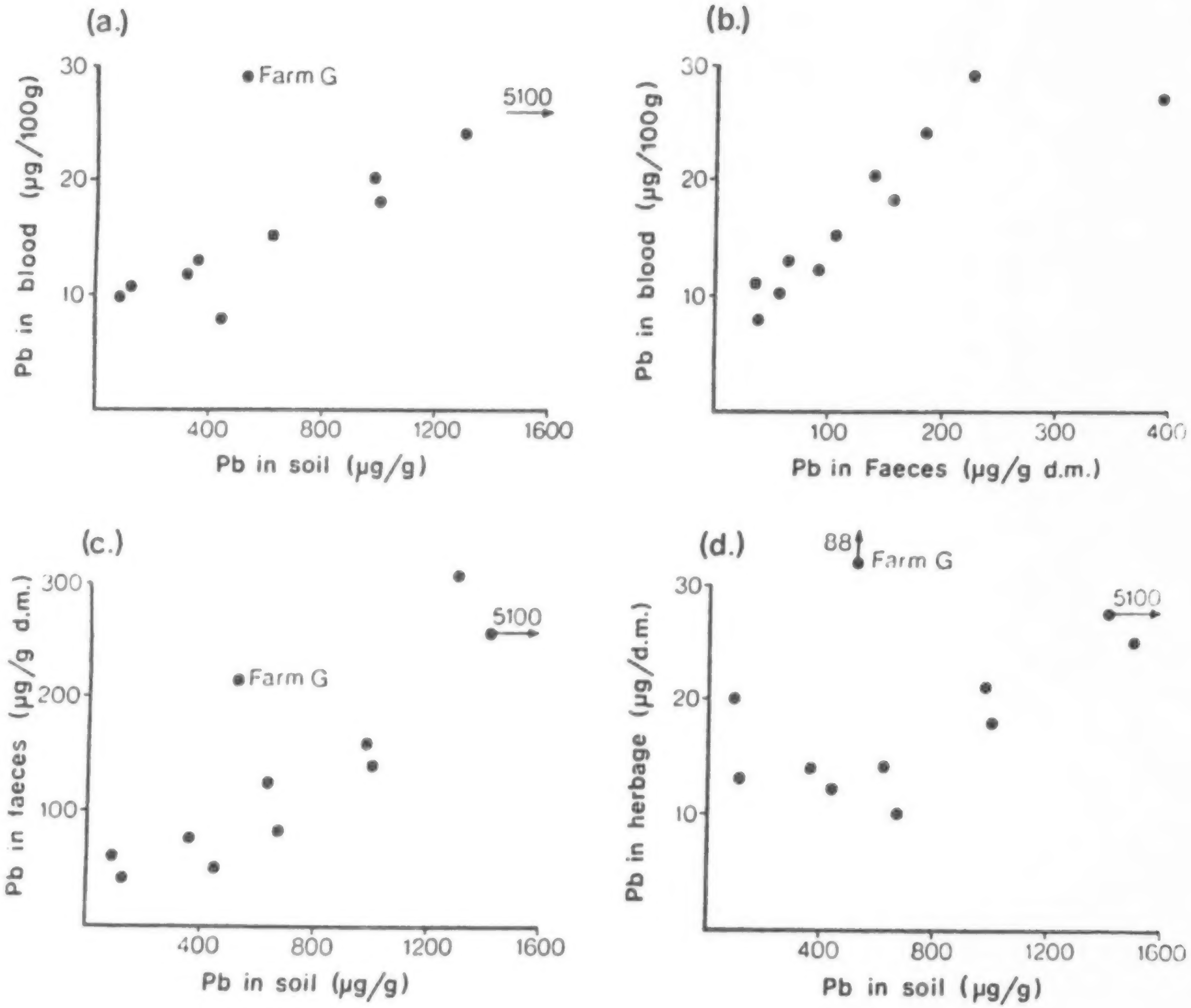

Figure 5. Relationships between the concentration of (a) mean bovine blood lead and mean soil lead, (b) mean blood lead and mean faecal lead, (c) mean faecal lead and mean soil lead, and (d) mean herbage lead and mean soil lead on 11 farms in Derbyshire, England.

The Role of Soil Ingestion

Grazing animals involuntarily ingest soil along with grass, and in Britain this may range from 1 to 18% of the dry matter intake of cattle and up to 30% in sheep (Field and Purves, 1964; Thornton, 1974). The amount of soil ingested will depend on the type of pasture, management factors, soil type, season and weather factors such as rainfall intensity (Healy, 1969). In the Derbyshire study noted above, where blood lead in cattle reflected lead in soil to a far greater extent than lead in pasture, it seems likely that direct soil ingestion should constitute an important pathway from the environment to the animal. Thornton and Kinniburgh (1978) investigated this using the element titanium as a stable marker, as this is present in soils in thousands of micrograms per gram and in grass at less than 10 μg g^{-1}. The rate of soil ingestion was estimated from the titanium concentration in the faeces as:

$$\%\text{ soil ingestion} = \frac{(1 - D_h)\, T_{if}}{T_{is} - D_h \times T_{if}} \times 100$$

where D_h is the fractional digestibility of the herbage and the subscript f refers to faecal concentrations. The results are summarized in Table 3, and clearly show that on the contaminated land lead ingested as soil was the main source to the animal, comprising around 70% of the intake. Soil contributed a far smaller proportion of the total intake of copper and zinc, which were not present as contaminants.

Table 3.

Mean contribution of soil to total daily intake of lead, zinc and copper in 11 herds of cattle in Derbyshire, England.

Farm Type (based on soil Pb in mg kg^{-1})	Mean % Soil Ingested	Soil Content (mg kg^{-1})			Total Daily Intake (mg day^{-1})			% Element Ingested as Soil		
		Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu
100-500 (n=4)	2.9	276	87	19	289	590	134	40	6	6
600-1000 (n=4)	3.7	856	311	37	621	860	170	71	19	11
1000-4000 (n=4)	2.9	2942	287	39	1700	714	152	66	15	9

Lead in the Urban Environment

Soils

In the UK it is now firmly established that the majority of urban soils are contaminated to varying degrees with metals. In London, England, Davies and co-workers (1979) reported a range of 42-1840 $\mu g\ g^{-1}$ EDTA-extractable lead. The values could be zoned according to proximity to the city centre: means for three zones were 523 $\mu g\ g^{-1}$ in the 0- to 4-km region, 242 $\mu g\ g^{-1}$ in the 4- 10-km region and 142 $\mu g\ g^{-1}$ in the 10- to 30-km region. A graph of soil lead against distance revealed a roughly exponential decline in values for soil lead from the city centre. A similar curvilinear relationship between the lead content of soil and distance from the city centre was found in Birmingham (England's second largest city) (Davies and Houghton, 1984).

It has been proposed that lead in vehicle exhaust fumes is probably the main source of soil lead contamination in urban areas. Other anthropogenic sources of lead and other metals in urban soils arise from industrial emissions, paint, contamination from bonfires and fossil fuel residues from open coal fires and soot commonly used as soil improvers and ameliorants, and pollution arising from the past use of urban sites (factories, gas works, scrap metal yards, etc.).

UK National Survey: A study of metals in urban soils and dusts was commissioned by the UK Department of the Environment in 1981 to establish the usual ranges of metal concentration to which the population may be exposed in the house and urban environment. Sampling was undertaken in 53 city boroughs, towns and villages in England, Scotland and Wales, selected to represent population weighting, geographical location and degree of industrial/urban development. Together with other environmental samples, surface garden soils (0-5 cm, composite of 25 subsamples) were collected from exposed surfaces around about 100 households in each location. The results for soils are summarized in Table 4 (Thornton et al., 1985). Amounts of lead, zinc and copper in urban garden soils were appreciably higher than those normally found in agricultural soils, confirming the results of several other studies in individual urban locations. Mean concentrations in London were higher than elsewhere. Examination of the data showed lower lead values in soil of houses under 30 years of age compared with those of 100 or more years of age. This probably reflects (i) voluntary reductions in the lead content of household paints, and (ii) a shorter history of soil contamination from various anthropogenic sources. The data for several 'geochemical hot spots' included in the survey are not shown in Table 4.

However, an example can be taken from old lead-mining villages in Derbyshire, where lead in 100 garden soils ranged from 1177 to 22,140 $\mu g\ g^{-1}$ (geometric mean 5605 $\mu g\ g^{-1}$). In this extreme situation over 93% of the soils exceeded 2000 $\mu g\ g^{-1}$ Pb, and the mean was nearly 25 times the national norm.

Table 4.

Concentrations of Pb, Cd, Zn and Cu in garden soils (0-5 cm) sampled in the UK reconnaissance survey (excluding 'geochemical hot spots') and in seven London boroughs (range and geometric mean, $\mu g\ g^{-1}$).

	Pb	Cd	Zn	Cu
Reconnaissance survey (n = 3550)	230 13-14125	1.2 1-17	260 13-14568	53 5-16800
7 London Boroughs (n = 579)	647 1-13680	1.3 1-40	424 58-13120	73 13-2320
Normal agricultural soils	10-150	1-2	25-200	2-60

It is possible that the long industrial history of the UK may present a special situation that may not be mirrored in other parts of the world with a shorter industrial record, alough similar results for lead have been found in Washington, DC (Preer et al., 1984) and the industrial city of Baltimore, Maryland, USA (Mielke et al., 1983).

Uptake into Vegetables. Several investigations have been undertaken into the uptake of lead into vegetables in UK urban gardens, as vegetable growing is regarded as a valuable source of fresh produce for the home as well as a leisure pastime. This section is limited to a summary of a preliminary study undertaken by my group at Imperial College restricted to 10 urban gardens in five locations.

The work was undertaken in the summer of 1983 with the aims of (i) determining the metal contents of garden soils and radish, lettuce and carrot grown in some typical urban areas, and (ii) attempting to apportion the metal contents of edible tissues to those derived from uptake from the soil and aerial deposition and soil splash. The urban locations investigated were London, Newcastle-on-Tyne, Leeds, Stoke-on-Trent and Scunthorpe. Experimental details have been previously described (Jones and Thornton, 1983). The vegetable crops were grown (i) directly in the local soil, (ii) in 20-cm-diameter pots with local soil, and (iii) in 20-cm pots containing a control 'uncontaminated' soil. Experimental sites were laid down as 9 x 4 randomized blocks in private gardens and allotments.

Metal concentrations in soils, radish and lettuce are shown in Table 5, and have been discussed in detail by Thornton and Jones (1984). Most of the soils were enriched in copper, lead and zinc, with the two London sites (4100, 2180 μg g^{-1} Pb) the most heavily contaminated, followed by those in Newcastle-on-Tyne; soils at older sites contained more metals than those recently developed. Concentrations of lead in radish and in lettuce increased with soil lead content ($r = 0.96$ and 0.97, respectively). It was concluded that lead in radish was largely due to uptake from contaminated soil. Between 40 and 80%

Table 5.

Pb, Zn and Cd in garden allotment soils (μg g^{-1}) and in radish and lettuce grown directly in the soils (μg g^{-1}, dry matter).

	Pb			Zn			Cu		
Location	Soil	Radish	Lettuce	Soil	Radish	Lettuce	Soil	Radish	Lettuce
London	4100	23.3	23.5	1562	267	144	2.8	0.7	0.8
	2180	11.9	16.4	2182	333	309	1.8	0.7	0.8
Newcastle-on-Tyne	840	12.2	9.4	506	65	97	1.4	0.4	0.6
	1608	7.3	8.5	660	52	101	1.8	0.5	0.6
Leeds	690	3.3	3.8	554	47	87	1.2	0.3	0.4
	136	3.2	4.1	190	26	76	0.6	0.6	0.7
Stoke-on-Trent	224	1.6	4.4	276	127	166	0.8	0.3	2.3
	90	1.5	1.7	174	50	99	0.6	0.2	0.8
Scunthorpe	108	1.4	2.0	258	42	81	0.1	0.2	0.4
	64	2.0	2.2	320	42	83	0.2	0.3	0.3
Control soil	92	-	-	160	-	-	0.5	-	-

of lead in washed lettuce at the London and Newcastle sites was apparently associated with foliar uptake or soil splash, as concentrations of lead in plants grown in the control soil at these locations were large. Chamberlain (1983) reviewed the subject of lead fall-out onto crops, and concluded that foliar deposition of airborne lead accounts for most of the lead in grasses and in other plants having a high leaf surface per unit mass. This criterion would apply to lettuce and other large-leaved garden crops such as cabbage, kale and spinach. In the present study, up to 75% of lead, nickel and iron was removed from lettuce by washing.

Dusts

The analysis of street, school playground and house-dust samples for lead has received considerable attention over the past decade. In general, there has been little attempt to standardize methodology in the numerous investigations undertaken. Procedures of sampling, sample preparation and analysis have varied considerably, and results cannot be accurately compared. Nonetheless, a general consensus of results points to the presence of elevated lead concentrations in dusts both within and external to the home. Guidance on acceptable levels of lead within urban locations has not generally been formulated, although the Greater London Council has adopted a guideline lead concentration in the 0.5-mm fraction of external surface dusts of 500 μg g^{-1} Pb as justifying further investigation, and 5000 μg g^{-1} Pb as justifying control measures (Duggan, 1981). Justification for the 500 μg g^{-1} Pb guideline is based on the recommendation that not more than 5 μg dL^{-1} blood should be attributable to the combined intake of airborne lead and lead in surface dusts. It was estimated that exposure to airborne lead at a concentration of 1 μg m^{-3} (commonplace in London) would account for one-half of this amount, and that 500 μg g^{-1} Pb in dust would result in a blood lead increment amounting to the remainder.

Ferguson and Ryan (1984) attempted to compare the multi-element composition of street dusts from large urban areas (New York and London) with that from small urban areas (Halifax, Christchurch and Kingston, Jamaica), and they concluded that the former contained more lead than the latter. However, only two samples were collected, each from an area of 1 m^2, in each city. A study of street dust by Harrison (1979) in Lancaster, a small town in northern England with little industrial activity, clearly showed the influence of traffic density on dust levels, with particularly high concentrations in garage forecourts and car parks (Table 6).

Table 6.

Concentrations of total lead in street dusts in Lancaster, England (mg kg^{-1} as collected) (from Harrison, 1979)

Site	Number of Samples	Range of Concentrations	Mean	Standard Deviation
Car parks	4	39 700-51 900	46 300	5 900
	16	950-15 000	4 5600	3 700
Garage forecourts	2	44 100-48 900	46 500	-
	7	1 370-4 480	2 310	1 150
Town centre streets	13	840-4 530	2 130	960
Main roads	19	740-4 880	1 890	1 030
Residential areas	7	620-1 240	850	230
Rural roads	4	410-870	570	210

One of the most detailed studies of lead in urban dusts to date was carried out in the small urban community of Champaign-Urbana in Illinois in the mid-1970s (Solomon and Hartford, 1976; Solomon and Natusch, 1977). Some 1400 dust and soil samples were collected at selected indoor and outdoor sites in both residential and non-residential areas of the community. Indoor dusts were collected with a specially constructed suction device over a 0.5 m x 0.5 m surface, allowing results to be reported both on concentration (μg g^{-1} Pb) and loading per unit area (μg m^{-2} Pb). In this study the methodology of sample collection and analysis is well documented. Results showed (a) the lead content of outdoor dust ranged from 600 to 1950 μg g^{-1} Pb and from 90 to 6649 μg m^{-2} in residential areas, (ii) much higher concentrations at non-residential sites, and (iii) mean lead levels in indoor dusts of 600 μg g^{-1} Pb and 680 μg m^{-2} in well-kept upper-middle-class residential interiors. The authors concluded that much of the lead was probably of automotive origin, although they also drew attention to the significance of lead-based paints. A comparison of rug-covered surfaces and wood tile surfaces in residential homes showed similar concentrations of lead in dusts from both, but larger loadings of dust (and therefore lead) from rugs (by factors ranging from 1.5 to 5).

UK National Survey. The survey referred to in the above section on urban soils also included comprehensive sampling of external and indoor urban dusts, and was primarily aimed at investigating the range of metal concentrations to which the general population was exposed (Culbard et al., 1983, 1986; Watt et al., 1983; Thornton et al., 1985). House dusts (taken from the householder's vacuum cleaner), surface garden soils (0-5 cm) and vegetable plot soils (0-25 cm) (where available) were taken from 100 households in each community, together with composite dust samples from 10 roads and five school playgrounds.

The methodology of this study is well documented, and it is worth noting that the samples taken for analysis were those passing through a 1 mm sieve for all dusts and a 2 mm sieve for soils. The main results for floor dusts, road dusts, playground dusts and garden soils are presented in Table 7. The mean concentration of lead (507 $\mu g\ g^{-1}$) in house dust was roughly similar to that reported in the Champaign-Urbana study, although the range of values extended much higher and the mean value (683 $\mu g\ g^{-1}$) for the London boroughs was significantly higher. The relationship between lead concentrations in house dusts and garden soils is highly significant (r = p 0.001) and is represented by the equation:

$$\log_{10} (\text{Pb-dust}) = 1.629 + 0.452 \log_{10} (\text{Pb-soil})$$

There is more lead in house dusts than in surface soil, indicating the possibility of internal sources of lead from within the home (such as paint lead piping, solder, etc.) supplementing those from outside, and/or the selective accumulation of fine (metal-rich) particles in the home transported from external sources such as fine soil particles and atmospheric aerosol. In excess of 2000 $\mu g\ g^{-1}$ Pb was found in 12% of the house dusts, and the distribution of lead in both house dust and soil was significantly related to the age of the property, with the majority of high lead concentrations associated with older homes. Lead in house dust was also significantly related to (i) the presence or absence of a regular home cleaner, (ii) the nature of the nearest road, (iii) the presence of high-lead paint, (iv) recent structural changes in the building, (v) current home decoration, (vi) the area of exposed garden soil, and (vii) the presence of a vegetable garden (Culbard et al., 1986).

Table 7.

Summary data for Pb, Cd, Cu, Zn in house dusts, road dusts, playground dusts and garden soil (0-5 cm) in the reconnaissance survey data (excluding 'geochemical hot spots') and the seven London boroughs ($\mu g\ g^{-1}$).

Reconnaissance Survey		House Dust	Road Dust	Playground Dust	Garden Soil
Pb	n = number of samples analysed	3953	335	186	3550
	Geo. mean*	507	707	269	230
	Range	13-34530	45-8860	11-4240	13-14125
Cd	n	3955	335	186	3549
	Geo. mean	6.8	1.7	1.8	1.2
	Range	< 1-804	< 1-28	< 1-68	< 1-17
Cu	n	3955	335	186	3551
	Geo. mean	204	75	44	53
	Range	3-48800	7-3030	3-1554	5-16800
Zn	n	3954	335	186	3550
	Geo. mean	1055	367	402	260
	Range	128-70100	46-22880	11-5424	13-14568
London Boroughs					
Pb	n	683	65	34	579
	Geo. mean	1007	1354	429	647
	Range	5-36900	172-9664	93-6860	1-13680
Cd	n	683	65	34	579
	Geo. mean	7.7	4.0	2.4	1.3
	Range	< 1-336	< 1-280	< 1-12	< 1-40
Cu	n	683	65	34	579
	Geo. mean	208	115	69	73
	Range	9-5300	18-2400	16-712	13-2320
Zn	n	683	65	34	579
	Geo. mean	1324	513	620	424
	Range	81-114800	121-5152	134-3738	58-13120

* The concentrations of metals in the samples analysed are distributed log normally. Thus the log geometric mean is presented as the best estimate of central tendency, together with the 100% range.

Davies et al. (1985) compared the composition of house dust with that of the outside garden soil in two villages in north Wales, one a control and the other in a severely contaminated lead mining area. The median soil lead concentrations in the control and contaminated areas were 70 and 1474 $\mu g\ g^{-1}$, respectively, and the corresponding median dust lead concentrations were 169 and 346 $\mu g\ g^{-1}$. The 95% probability range for dust lead in the control houses was 36-873 $\mu g\ g^{-1}$, and in the contaminated village the 95% range was 56-2061 $\mu g\ g^{-1}$. Lead levels in dusts and soils were positively correlated ($r = 0.517$, $p = 0.001$, $n = 90$) for the log-transformed data, and the regression equation was calculated as:

$$\text{Dust-Pb} = 0.30\ \text{Soil-Pb} + 1.65$$

It was concluded that, for the original arithmetic data, each 10-fold increase in soil lead corresponded to a doubling of dust lead.

Source Apportionment Studies. To date, attempts to identify the sources of lead in external and indoor dusts have met with limited success, and I am not aware of any study which shows conclusively the proportion of lead in dust derived from lead paint or vehicle emission.

Harrison et al. (1981) used a sequential extraction procedure to characterize metals from street dusts into five fractions termed exchangeable, carbonate, iron/manganese oxide, organic and residual. Lead occurred mainly in the carbonate and iron/manganese oxide phases, and the authors considered this moderately bio-available.

Gibson and Farmer (1984) also studied the chemical form of lead in dusts. They used a six-step sequential leaching procedure to partition lead and other metals in 60 Glasgow street dusts into exchangeable, carbonate-bound, easily reducible, moderately reducible, organic and residual forms in an attempt to characterize environmental mobility and bioavailability. They concluded that the combined exchangeable, carbonate and easily reducible fractions were 'broadly related' to that extracted by 0.07 M HCl, "commonly considered to approximate to human stomach acidity".

Solomon and Natusch (1977) developed a scheme of dust characterization based on different size fractions, densities and magnetic properties, and using external dusts from sites characterized by high traffic levels (12,000 to 20,000 cars per day). They found that (i) lead concentrations in dust were highest at the curb and at the building line at two sites where high-lead paint was present--at two other sites without lead paint, levels decreased from the curb to the building, (ii) the concentration of lead generally increased with decreasing dust size, with maximum concentrations in the smallest size fraction analysed (1.45 µm), and (iii) the total amount of lead in the less than 45-µm material increased with distance from the road curb. The authors attempted to use multi-element analysis as a means of source apportionment, and provided some preliminary evidence of the potential use of lead:bromine ratios to differentiate sources of lead where the principal components are from traffic and from paint. In dust samples taken from gutter, curb and building line, large amounts of lead were found in the dense fraction, especially in the non-magnetic part. The authors concluded that (i) automobile exhausts were the source of lead found in curb and near-curb regions, and (ii) significant contributions from leaded paints near the building line (around 40% of the total lead) were associated with the 90- to 600-µm dense non-magnetic fraction. Density and magnetic tests and multi-element analysis of indoor dusts proved inconclusive.

Linton et al. (1980) described in detail a method identifying the sources of lead-containing particles in urban dusts using scanning electron microscopy (SEM) and energy dispersive X-ray analysis. They concluded that (i) the technique provides an excellent definition of the probable sources of individual lead-containing particles, and (ii) the ability of the technique to establish the amounts of lead derived from each source is poor, because of difficulties associated with quantitative determination of lead in individual particles.

Johnson et al. (1982) described a similar technique of dust characterization for lead source apportionment using SEM with automated image analysis and X-ray energy spectroscopy. The method applied to house dust samples was carefully described, and the authors concluded that the technique shows considerable promise; using the comparison of the elemental composition associations of house dust classified into specific categories with elemental association of a library of specific source samples, the 'signature' of the dust sample could be apportioned by computer into the best fit of known components. Studies based on this methodology are continuing at Imperial College, London, and different types of lead-bearing particles have been described in house dusts from Birmingham, England (Johnson et al., 1985).

Exposure from Soil and Dust

It has been proposed that direct ingestion of soil and dusts by children is likely to contribute an important source of lead exposure; hand-to-mouth activity by the young child during meals and at play is considered to be of particular significance. The Royal Commission on Environmental Pollution (1983) stated, "we believe that the intake of lead from dust can be substantial for young children". Estimates of intake by this route are, however, based on a number of assumptions and too few actual measurements. Seasonal differences of time spent on play outdoors and indoors, the presence or absence of a garden and the quantities of lead in soil and in dust actually transferred to the mouth from the hand would seem to be factors of significance for which there are few reliable data.

Direct intake of soil is poorly documented, although it has been shown that soil lead significantly influenced blood lead of children between the ages of 3-6 years in the vicinity of a smelter, with a 4% increase in blood lead per 1000 μg g^{-1} increase in soil lead at the age of 6 (Walter et al., 1980).

It has been documented that repeated ingestion of as little as 0.4 g of street dust containing 2000 μg g^{-1} Pb can eventually result in clinical lead poisoning in young children (NAS, 1972).

Day et al. (1979) made a "small" number of direct measurements on the transfer of dirt from the hands onto a "typical" sticky sweet, and concluded that an ingestion of 100 μg Pb contained in 100 mg of average dust could result from the consumption of 2-20 sweets in a school playground; ingestion of 20 "badly contaminated" sweets could contain 1000 μg Pb.

Solomon and Hartford (1976), accepting that a child could be expected to have 10 mg dust on his fingers, calculated that if the child were indoors and placed his fingers in his mouth 10 times, an average of 60 μg Pb per day might be ingested. They postulated that if the child spent considerable time outdoors or in a non-residential setting, these values could be doubled or tripled. Solomon and Natusch (1977), again using the 10 mg dust and 10 times sucking principle, arrived at values of daily ingestion of 100 μg Pb indoors and 1020 μg Pb outdoors!

Duggan and Williams (1977) attempted to measure the amount of dust retained on the pulp of a forefinger and thumb, showing an average of 4 mg dust (range 2-7 mg). Again they used the 'arbitrary' figure of 10 suckings a day during street play, and arrived at an estimate of 20 mg dust ingested per day. Taking 1000 μg Pb g^{-1} as the average lead concentration in London street dust, they then doubled these figures to a probable range of intake of 20-200 μg Pb and, influenced by the estimates of other workers, chose an average value of 50 μg Pb per day. They quite rightly drew attention to the fact that there are no data which quantify the biological availability of lead in ingested street dust.

Some attempts have been made to determine the bioavailability of soil and dust lead using rats. Dacre and Ter Haar (1977) found soil lead about 70% as available as lead acetate; Stara et al. (1973) found street dust lead to be as available as lead acetate; Levander et al. (unpublished data quoted in Chaney and Strickland, 1984) found the bioavailability of garden soil lead from five different urban gardens to range from 16 to 70% of that of lead acetate.

Vostal et al. (1974) measured the quantity of lead on the hands of suburban and city children as 5 and 20 μg, respectively (median values). Using the assumptions made by Duggan and Williams (1977), this would imply daily intakes of 8 μg Pb for suburban children and 33 μg Pb for city children.

A more detailed assessment of the significance of dust as a possible source of lead exposure for young children through hand-to-mouth activity has recently been undertaken in the city of Birmingham, England (Thomas et al., 1985). The study was based on 97 volunteered children selected from a representative sample of 2-year-olds born and still resident in the city centre.

Comprehensive sampling of dust, soil and air was undertaken in the home of each child, and hand-wipe samples together with duplicate samples of the child's diet (food and water) were collected on seven consecutive days. Video films were taken in each home for a total of approximately 4 h to quantify mouthing activity. The results are still being collated, and it is intended to calculate lead intakes from all sources (including dusts) and to relate those to lead in venous blood.

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13. THE POTENTIAL FOR HEAVY METAL EXPOSURE FROM URBAN GARDENS AND SOILS

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Introduction

In 1978, the Cornell University Extension Service Urban Garden Program held a conference in New York City to evaluate the potential problems for urban gardening if air or soils are enriched in heavy metals such as lead. At that conference, work of Preer and Rosen (1977) and Spittler and Feder (1979) was presented, indicating that lead paints can contaminate urban garden soils and vegetable crops. Before that conference, little consideration had been given by the agricultural community to potential health effects of contaminated urban soil. Many scientists had considered contamination of crops by automotive lead emissions, sewage sludge, smelter emissions, pesticides and metal-enriched manure. This new information has affected the way we must view potential lead problems in urban areas, including urban gardening.

Several related lead poisoning issues were also undergoing increasingly intense research in the later 1970s, and the research suggested greater risk to children from lead in urban soils than had been previously recognized; these risks included lead exposure by inadvertent ingestion of house dust, and neurobehavioural impairment in children at lower lead exposures than previously indicated as causing health effects. This review considers the relationships of lead exposure from urban soils and dusts and from crops grown in urban gardens, and the potential consequences of that exposure. It considers the sources of metals in urban soil and dust, how these can be economically tested for and the potential consequences on garden productivity and child safety regarding lead poisoning. We also consider pathways from soil to humans, via both plant uptake of metals and soil ingestion by children.

Why have these questions become relevant? The connection results mainly from modern interest in vegetable gardening. Gardening has become popular in nearly all socio-economic groups in the US. Because people are doing more gardening in urban areas, the processes that cause heavy metal enrichment of soils, plants and people in cities must be reconsidered. Although there is little evidence that most gardeners are at risk, it is clear that gardeners in some inner-city areas, near some industries and in some cities where highly polluted sewage sludges were given away are at enough risk to need information to protect themselves or their children. Further, because nearly all soil pollution is anthropogenic (resulting from human activities), individuals would be wise to obtain garden and house-side soil tests before they begin gardening, and probably before they purchase a house or rental unit or move children into such a house. The need for soil tests is slight for suburban areas, but much higher in the inner city or if lead paint could have been used.

In the last 15 years, much research has been conducted on sources of heavy metal pollution, pathways for movement of soil or airborne metals to humans and potential health effects of these metals. Some important questions remain unanswered, and the present review cannot be comprehensive about these many areas of research.

Food-chain Pathways for Urban Heavy Metals

As reviewed below, many different sources can contribute heavy metals to urban air and soil. Most of these sources can apply to suburban and rural areas as well, although the effects of automotive and smelter emissions are of course less intense at greater distances from the source, so the more remote areas are at less risk.

The two key processes which allow human exposure to metal pollution through gardening are plant uptake where the plant is human food, and soil ingestion. Plant uptake includes both absorption of air pollutants on plant surfaces and uptake by the roots with translocation to edible plant tissues. Soil ingestion includes either pica, the intentional ingestion of non-food objects, or inadvertent soil ingestion during hand-to-mouth play or when taking snacks and meals without prior hand-washing.

Plant Contamination by Automotive Emissions

The initial focus on lead was contamination of crops grown near highways. Cannon and Bowles (1962) reported lead in garden soil and vegetables in one of the very first papers on automotive lead pollution. Lead bromide is released to the air from automobile exhaust, but lead sulphate is quickly formed and precipitated (Olsen and Skogerboe, 1975; Biggins and Harrison, 1979). Aerosol lead is apparently absorbed from the air by surface tension of leaf surfaces, and is not readily remobilized from the leaf by wind (Wedding et al., 1975, 1977; Carlson et al., 1976). Lead chloride is soluble, and therefore much of it can be rinsed from leaf surfaces (Carlson et al., 1976), but automotive lead on leaves near roadways is mostly lead sulphate. Washing these leaves with water removes only about 50% of the lead present (Preer et al., 1984).

Several research groups have studied the potential of roadside trees to reduce lead pollution of crops. Heichel and Hankin (1976) noted that white pines removed much lead; the trapped lead increased soil lead under the trees over time. Collet (1978) found a reduction in lead levels in vegetable crops if a row of trees grew between the highway and crops. Many researchers have measured the lead concentration of crops grown at different distances from highways with different traffic density. The higher the traffic density, the higher the crop lead. Crops with hairy leaf surfaces retain more aerosol lead than crops with smooth leaf surfaces. Many fruits have smooth surfaces and low lead levels. Lead deposition falls logarithmically with distance from the highway (Shuck and Locke, 1970; Motto et al., 1970; Page et al., 1971; Ward et al, 1975; David and Williams, 1975). Therefore, more lead is deposited close to the road, at least partly because larger particles settle out sooner and nearer to their source. This is difficult to interpret in urban areas, where streets surround all four sides of a community garden or housing.

Roadside crop contamination has been extensively evaluated (EPA, 1977). The amount of lead on a leaf surface depends on distance from the road, crop species, time exposed before harvest and recent rainfall (Crump et al., 1980; Crump and Barlow, 1982). Rapidly growing leafy crops, if properly washed before consumption, are not an important source of lead for children. These crops are significantly higher in lead than crops sampled in rural fields (Wolnick et al., 1983), but often not different in lead from crops marketed in urban areas. Marketing in urban areas exposes fresh vegetables to contamination by urban dust rich in lead. Based on analysis of ^{210}Pb in foods and faeces, Chamberlain (1983) estimated that fall-out lead contributed less than 15% of adult dietary lead.

Plant Uptake of Heavy Metals

Soil-Plant-Barrier Model

Plants absorb different elements from different soils, and the levels absorbed are related to element properties, soil properties (pH, element level in soil, organic matter, cation-exchange capacity (CEC) and level of other elements in the soil) and plant properties (plant age, species, edible portion). The accumulation of different elements has been reviewed extensively by Logan and Chaney (1984).

In short, some elements are easily absorbed and translocated to food-chain plant tissues (e.g. Zn, Cd, Mn, Mo, Se), while others including lead are not. Some elements are strongly bound or precipitated in the soil, or in the fibrous plant roots, and are not translocated to plant foliage in injurious amounts even when soils are greatly enriched (Pb, Fe, Hg, Al, Ti, Cr, etc.). Other elements are easily or relatively easily absorbed and translocated to plant foliage, but phytotoxicity to the crop may limit plant levels of the element to levels safe for chronic ingestion by animals (Zn, Cu, Ni, Mn, As, B). These processes have been collectively labelled the "soil-plant barrier" (Chaney, 1980). The exceptions to the protection of the food-chain by the soil-plant barrier are (i) soil ingestion, and (ii) the elements Cd, Se and Mo. For urban gardens, this means soil ingestion which can allow excessive acute or chronic lead ingestion in some cases, and crop uptake of cadmium which can allow excessive chronic cadmium ingestion.

Plant Uptake of Lead - General

During the last 15 years researchers have improved the techniques needed to conduct more valid research on plant uptake of elements (Logan and Chaney, 1984). Examples can easily be found in the lead, cadmium or phytotoxicity literature. When soluble lead salts [$PbCl_2$; $Pb(NO_3)_2$] are added to soils, the anion temporarily increases lead solubility. The high ionic strength reduces metal sorption by the soil. Lead-complexes may form and keep lead soluble. The metal addition can substantially lower soil pH as the metal reacts with the soil. More lead is taken up in pot studies than field studies. Zimdahl et al. (1978) studied the effect of adding different lead compounds, and found much more lead was absorbed by five crops from $Pb(NO_3)_2$- than $PbSO_4$-amended soils. When soluble lead salts are added to soils in pot studies, higher soil pH or higher soil CEC reduces lead uptake (MacLean et al., 1969; Cox and Rains, 1972; Miller et al., 1975a, b). The effects of lime or CEC are usually attributed to greater absorption of the lead by the soil under the conditions which reduce plant lead. Added phosphate, manure, limestone or sewage sludge compost can reduce plant uptake of lead (MacLean et al., 1969; Cox and Rains, 1972; Zimdahl and Foster, 1976; Judel and Stelte, 1977; Scialdone et al., 1980; Chaney et al., 1982; see also Table 3). Soils deficient in phosphate or sulphur show strong reduction in plant lead when these elements are added (Jones et al., 1973). However, few urban soils are low in phosphate, and none low in sulfur. When lead salts have a longer period to react with the soil, or when lead salts are applied in the field (Baumhardt and Welch, 1972) rather than to pots of soils, much lower lead uptake occurs. Hassett and Miller (1977) grew corn on roadside soils in pots, and found much lower lead uptake than from the $PbCl_2$-amended soils studied by Miller et al. (1975b). These studies demonstrate the need for care in selecting research methods which represent long-term availability of environmental lead to plants.

Lead uptake in the field shows a seasonal variation. Mitchell and Reith (1966) found lead in orchard grass and clover rose in the fall and winter by as much as 10-fold due to soil contamination, and their evidence did not support an aerosol source. Haye et al. (1976) evaluated this seasonal response further, and found it even in a growth chamber with filtered air. Research has been conducted to examine whether slow growth during cold weather simply increases the total exposure time of leaves to aerosol lead, or whether simple plant uptake explains these seasonality findings. Ratcliffe and Beeby (1980) found decaying grass leaves absorbed more soluble lead than young growing leaf blades. Crump et al. (1980) found seasonal increases in lead concentration in perennial ryegrass. Young leaf blades harvested at any time of year had similar lead levels at a specific location, but old leaf blades were up to 10-fold higher in lead. Crump and Barlow (1982) used bags of sphagnum peat moss and bags of cut grass leaves to assess seasonal patterns of deposition of aerosol lead. Moss accumulated more lead in winter than summer, apparently due to seasonal wind speed differences. However, lead levels in grass growing during a 30-d period and lead caught in moss bags during the same 30 days were very comparable. Thus, the continuing accumulation of lead in old leaf blades appears to explain the seasonal pattern of lead in pastures and roadside crops. These results have few implications for garden crops, except supporting the need for careful washing of leafy vegetables.

Plant Levels of Lead in Urban Gardens

Although all evidence indicates that inadvertent soil ingestion allows much greater lead exposure than eating garden vegetables grown on the soil, plants grown in urban gardens which are highly contaminated with heavy metals may contain elevated metal levels in their edible portions. To examine the influence of urban gardening on plant uptake of metals, two approaches have been used: (i) bring garden soils to a clean air environment for pot study of metal uptake and (ii) grow crops in gardens and analyse. Davies (1978), for example, chose to grow radish in many gardens. Since the influence of aerosol lead on lead levels in this root crop is minimal, soil lead availability could be evaluated.

Preer and Rosen (1978) reported significantly higher crop lead and cadmium when crops were grown in a community garden over an old landfill where soil lead was the predominant lead source. Spittler and Feder (1979) grew several vegetables in replicated beds of urban garden soils, and found very high lead in lettuce and root crops. Preer et al. (1980a) sampled leafy vegetables and soil (10-1400 μg g^{-1} Pb; mean 200 μg g^{-1}) in Washington, DC, gardens. Although crop lead was correlated with soil lead, it was more highly correlated with average daily traffic/distance from road. In this study, plant lead averaged only 4.5 μg g^{-1} (range 1-12 μg g^{-1}) (dry-weight basis). In a subsequent study of downtown Washington, D.C. gardens, Preer et al. (1984) found appreciably higher soil lead (44-5300 μg g^{-1}; mean 680 μg g^{-1}), and slightly but significantly higher leafy vegetable lead (6.4 μg g^{-1}). However, plant lead was not linearly correlated with soil total lead. Preer et al. (1980b, c) reported analyses of many crops and effects of soil pH and traffic on plant lead and cadmium in urban gardens. As expected, fruits are always much lower in lead than leafy or root vegetables; leafy crops are usually higher than root crops, but this comparison is affected by soil lead level. Collards and kale are lower in lead than lettuce, chard and beet greens.

Hibben et al. (1984) attempted to separate air and soil factors by creating soil beds from urban and suburban soil at urban and suburban locations. The soils used contained only 66 and 273 μg g^{-1} Pb, and a substantial difference in fertility confounded the study. In 1 year, the urban location caused significantly higher lead in leafy crops but not root crops, even though they were grown relatively distant from traffic. The higher lead in soil caused a small but significant increase in lead in leafy crops. Kneip (1979) analysed several crops grown in demonstration gardens in New York City. Soil lead was below 500 μg g^{-1}, and some of these demonstration gardens had fresh soil when they were begun. Crop lead was compared with lead in crops from markets and the FDA analysis of lead in foods. Kneip concluded that, for these gardens, the crops would add little dietary lead compared with market crops.

A few studies have been conducted with garden soils very rich in lead. We sampled collard (washed with care of home cook) and soils from 50 inner-city gardens in Baltimore, MD. Table 1 shows the results. Plant lead concentration was significantly related to log-transformed soil total lead concen-

Table 1.

Heavy metal levels (μg g^{-1}) in soils and collards from 50 Baltimore urban gardens.*

Factor	Mean	SD	Geo. Mean	Min.	Med.	80th	Max.
Soil Pb	1171	1889	586	46	573	1450	10900
Soil Cd	2.50	2.55		0.28	1.72	3.06	13.6
Soil Zn	588	815		20.6	352	751	4880
Soil Cu	78	67		5.8	54	120	293
Soil Ni	6.3	4.6		1.6	4.9	7.8	25.2
Soil Mn	167	90		28	140	238	386
Soil pH	6.19	0.60		4.51	6.28	6.66	7.17
Plant Pb	6.63	2.34	6.26	2.60	5.9	8.4	13.4
Plant Cd	0.80	0.66		0.10	0.54	1.10	2.91
Plant Zn	192	150		31.9	165	256	621
Plant Cu	7.2	7.0		2.5	5.1	8.5	48.5
Plant Ni	1.7	1.8		0.10	1.4	2.0	11.6
Plant Fe	104	70		44	79	130	463

* Soil method: 1 N HNO_3, 5 g/50 mL, 2-hr extraction.
Plant method: Dry ash, HNO_3, HCl.

tration. Collard lead was only 6.6 μg g^{-1} (range = 2.6-13.4 μg g^{-1}). In later studies, lettuce lead was appreciably higher, and unrelated to soil lead. We believe this indicates aerosol deposition usually exceeds soil as the lead source for lettuce, collards and other leafy vegetables growing in urban gardens.

One pot study of lead uptake was conducted using Baltimore urban garden soils. 'Tania' lettuce was used in this research because Feder et al. (1980) found this cultivar to accumulate more lead than others grown on an incinerator ash rich in lead (Table 2). The ability of NPK fertilizer, limestone, high phosphate fertilizer or sewage sludge compost to reduce crop lead uptake was evaluated (Table 3). In general, lettuce lead remained at acceptable levels where NPK fertilizer was applied. Elevated lead levels were found in lettuce grown on a garden soil with 5210 μg g^{-1} Pb. For the high-lead soil (5210 μg g^{-1}), phosphate or sludge compost in addition to NPK fertilizers were more effective in reducing lettuce lead than NPK fertilizer alone. Healthy lettuce was grown on all soils and treatments.

Nicklow et al. (1983) evaluated lead uptake by six crops grown on a control soil, a high-lead urban garden soil or a 1:1 mixture of these soils. Plant lead was linearly related to soil lead, probably because only one soil lead source was studied. Lettuce and turnip greens were highest in lead. Collard and kale were relatively low in lead even with the very high soil lead. Beet, turnip and carrot also accumulated lead, with very high levels in the peel. Soil fine particles adhering to root crop peels can contribute substantial lead. Root crops must be washed and peeled to reduce crop lead to acceptable levels for about 10% of urban gardens, those rich in lead.

Davies and co-workers have found radish and lettuce can be significantly

Table 2.

Difference among lettuce cultivars in lead accumulation from control and incinerator ash-amended soil.*

Cultivar	Pb in Lettuce Shoots ($\mu g\ g^{-1}$ dry weight) Incinerator Ash	Control	Difference
Tania	27.4	8.6	18.8
Butterhead 1044	22.6	5.6	17.0
Butterhead 1034	22.6	10.6	11.3
Summer Bibb	21.5	9.3	12.2
Butterhead 1033	20.2	5.7	14.5
Buttercrunch	15.0	6.4	8.6
Belmay	12.6	11.0	1.6
Dark Green Boston	10.7	8.6	2.1
Valmaine	10.6	4.0	6.6
Soil Pb (1 N HNO_3)	5585	46	-
Soil pH	7.8	5.8	-

* In co-operation with Dr. W. Feder, University of Massachusetts.

Table 3.

Effect of amendments on lead concentration in 'Tania' lettuce grown in six soils in a growth chamber.

Treatment	Pb in Lettuce Shoots ($\mu g\ g^{-1}$ dry weight) at Soil Pb Concentration ($\mu g\ g^{-1}$) 12	392*	413*	655*	1334*	5210*
Control	2.8a**	4.6a	15.7a	4.7a	17.7a	37.8ab
NPK	2.0a	4.1a	3.8ab	7.6a	8.4a	26.6bc
NPK + $CaCO_3$	1.8a	5.0a	9.3ab	6.4a	6.0a	43.7a
NPK + P	2.9a	9.3a	4.4ab	9.4a	10.5a	17.ac
NPK + 5% compost	2.2a	5.1a	2.4b	4.8a	6.5a	16.1c
NPK + 10% compost	2.6a	3.5a	2.8b	5.5a	5.3a	19.7c

* Urban garden soils from Baltimore, MD.
**Means within columns followed by the same letter are not significantly different (P<0.05) according to Duncan's New Multiple Range Test.

and unacceptably high in lead when grown in high-lead urban gardens, or high in lead or cadmium in gardens influenced by mining and smelting wastes (Davies and Roberts, 1975; Davies, 1978; Davies et al., 1979; Davies and Ginnever, 1979; Davies and White, 1981; Davies et al., 1981).

Looking at the whole data base, it would appear that crop lead is not yet a significant limitation for growing vegetables in a garden with 500-1000 μg g^{-1} soil total lead (crops washed; root crops peeled). However, this much soil lead, when present in areas frequented by children, can significantly contribute to blood lead in children. Gardens very high in lead (e.g. 3000 μg g^{-1}) could be used to safely grow fruits and grain crops, but not leafy or root vegetables. For these high-lead gardens, extreme care would be needed to reduce soil transfer to house dust and minimize exposure of children, and in a practical sense this would require too much care for routine gardening to be considered safe.

Ingestion of Metals in Soil and Dust

When soils are contaminated with metals, soil ingestion can become an important exposure pathway for heavy metals. Soil ingestion by farm livestock was initially identified as the source of excessive tooth wear. Plants become contaminated by soil by (i) rainfall splash, and (ii) trampling by the livestock. Cattle and sheep could eat as much as 24% soil in their dry diet under worst-case, very poor management. Soil is normally only about 1-2% of the diet (Fries et al., 1982).

Cattle have been lead-poisoned when grazing soils naturally high in lead (Harbourne et al., 1968; Egan and O'Cuill, 1970; Thornton and Abrahams, 1981). When a lead smelter contaminated a pasture, lead-enriched crop residues remained on the soil surface even after the smelter closed. Cattle blood lead fell to normal levels only when the sward surface thatch was incorporated into the soil to prevent direct ingestion by the cattle (Edwards and Clay, 1977). Inadvertent soil ingestion is an important source of exposure when plant uptake of an element is small compared with soil concentrations (e.g. Pb, As, Cu, F, Hg, toxic organic compounds, etc.).

Children of Lead Industry Workers

In the late 1970s, the lead poisoning of children of lead industry workers became an important example of inadvertent soil and dust ingestion. Baker et al. (1977) studied workers' children and their neighbours at a secondary lead smelter where the workers had not changed or showered at work. The housing was relatively new, and without lead-rich paints. House dust contained 404 $\mu g\ g^{-1}$ Pb in the neighbour's homes, but 2690 $\mu g\ g^{-1}$ in the workers' homes. Blood lead correlated well with lead level in house dust, with 10 children needing chelation therapy to remove lead. Similar results were reported by Dolcourt et al. (1978). Giguere et al. (1977) studied a smelter where workers changed clothes at work and showered, but brought their clothes home to wash. Blood lead was not as high, but lead in house dust was an important source. Rice et al. (1978) looked at smelters where workers showered at work and work clothes were washed at work. House dust lead was still significantly higher in workers' homes. The authors believed that workers' street clothing, shoes and cars became lead-contaminated, and the lead-rich dust was transferred to their homes. Millar (1978) also found higher blood lead in children of lead workers in the UK. Archer and Barratt (1976) measured lead in "white cotton socks" given to employees at a secondary lead smelter to study contamination of clothing. Although factory workers' socks had the highest lead levels, supervisors' and administrative workers' socks were also lead-exposed. Simply walking through the factory contaminated shoes socks, and pant legs. Fergusson et al. (1981) confirmed these contamination pathways.

We believe that these observations are of great importance. They allow separation of the lead in house dust relationship to children's blood lead from the other socio-economic factors which ordinarily confound studies of urban children. In this research model, children lived in homes with or without high levels of lead in the house dust. Simply living in these homes caused the children to ingest lead-laden dust which led to higher blood lead.

Research on multimedia lead exposure has difficulty separating out a single factor for study, but the workers' children serve this critical logical purpose. No one can neglect housedust lead exposure to children after reading the literature on lead workers' children. The Occupational Safety and Health Administration (OSHA) subsequently required that workers shower and change clothes before leaving work, with the work clothing washed at the factory (even though the Rice et al., 1978 and Archer and Barratt, 1976 papers show this cannot completely prevent carrying home the factory dust which is rich in metals).

Increased Blood Lead in Children Ingesting Urban Soil and Dust

As noted above, the literature on increases in blood lead in children who ingest lead-enriched soil and dust has grown rapidly in the last decade. A detailed reading of the literature on children blood lead levels and heavy metals in urban soil and dust shows that although some authors believed specific lead-poisoning cases were caused by soil lead, medical specialists could not identify the importance of this source until the incidence of lead poisoning due to ingestion of lead paint chips had decreased. The increased blood lead in urban versus suburban and rural children led some researchers to consider the dust lead path (Cohen et al., 1973; Sayre et al., 1974). The connection between smelter lead emissions in soil and dust and blood lead in children has been an important lesson, and a difficult political problem. Finally, the lead ingestion by children of lead workers, noted above, attracted the attention of most researchers studying lead poisoning in children.

Around lead smelters, soil and house dust become greatly enriched in lead. A very high incidence of excessive blood lead was found at many smelter towns (Roberts et al., 1974; Landrigan et al., 1975; Yankel et al., 1977). In Belgium, Roels et al. (1980) studied children of several age groups over a period of years during which smelter lead aerosol emissions were nearly eliminated. However, soil and dust remained lead-enriched. Roels et al. (1980) reported that blood lead fell quickly in teenagers and adults when air lead fell; however, blood lead fell only slightly in young children, demonstrating the predominance of ingestion of soil and dust lead rather than inhalation of aerosol lead.

In 1974, Needleman and Shapiro reported unusual tooth lead and blood lead levels in a group of parochial schoolchildren in Philadelphia who attended a school near a factory which emitted lead. Dust in the playground and school was very rich in lead. Children with low lead exposure at home had high lead exposure through soil and dust at school, and consequently had higher body burdens of lead. The Omaha, Nebraska (Angle and McIntire, 1979) and Arnhem, Netherlands (Brunekreef et al., 1981), lead studies, where smelters are an important source, also found soil and house dust were very important sources of lead exposure.

Methods were developed to better estimate lead exposure via house dust.

In one approach, Vostal et al. (1974) and Sayre et al. (1974) used an alcohol towelette or 'wipe' to wash children's hands or house surfaces to estimate the quantity of lead per hand or per square foot of surface of floor, wall or windowsill. Baker et al. (1977) used pre-weighed cotton balls, and Lepow et al. (1974) used pre-weighed adhesive labels to obtain weighed samples of dust, and could thus estimate lead concentration in surface dust. As will be shown below, both results are important.

It became evident that house or hand dust lead was related to blood lead in some children (Sayre et al., 1974; Lepow et al., 1975). Charney (1982), Duggan (1983) and NAS (1980) summarized these data. Independently, Shellshear (1973) and Shellshear et al. (1975) came to a similar conclusion, and connected the soil and dust lead exposure to exterior paint. Children who played in high-lead soils, or who had pica for lead-enriched soils, had higher blood lead. Many specific cases of soil lead as the source of lead poisoning have been noted, again often for soils enriched in lead from exterior paints (Orton, 1970; Fairey and Gray, 1970; Hardy et al., 1971; Galke et al., 1977; Wedeen et al., 1978; Charney et al., 1980; Stark et al., 1982; Mielke et al., 1984). Yaffe et al. (1983) connected the paint-to-soil-to-blood pathway with lead isotope ratios (sites studied appear to have had low automotive lead exposure). Of course, some to much of the lead in house dust can come from automotive exhaust and fine particulate paint residues (e.g. Sayre and Katzel, 1979), and much of the effect of automotive lead emissions is believed to result through dust or soil ingestion (Millar and Cooney, 1982).

Another argument supporting lead in soil and dust as one lead source for children is recent examination of lead in faeces. When paint chip lead was still a frequent cause of lead poisoning, X-ray examination of intestines or faeces revealed many opaque chips. The paint chips were not completely disintegrated during digestion. The massive educational programme about paint chip lead greatly reduced the incidence of overt lead poisoning. A recent re-examination of faecal lead found a relatively even distribution rather than discrete chips in most cases (Hammond et al., 1980). This indicates a fine particle size lead source, such as lead in soil and dust.

As will be discussed below, absorption of lead from urban soil and dust depends on (i) nutritional factors, (ii) amount of soil and dust lead ingested, and (iii) concentrations of lead in the ingested soil and dust. This severely complicates attempts to correlate exposure and blood lead. Blood lead depends on many socio-economic factors, factors which affect nutritional status, child supervision and house dust lead levels (Stark et al., 1978, 1982b; Charney et al., 1980).

One of the most important new findings is the report of Charney et al. (1983). Controlling house dust by regular cleaning reduced dust lead per unit surface area, and also significantly lowered blood lead in children living in these cleaner homes. Cleanliness is important when one lives in a lead-rich environment where soil and dust can be important lead exposure sources. In the recent Yaffe et al. (1983) study, poor plumbing caused house dust lead levels to be very high, which in turn contributed to the raised blood lead in children.

The quantitative relationships between lead concentration in house dust, amount of house dust lead per unit surface area and blood lead levels vary among study populations depending on other lead sources and human behaviour. Among the child-specific factors which affect these studies were: Did parents make children wash their hands before eating? Did children suck their thumbs or fingers? Did children play in lead-rich soils? Did parents clean the home regularly? Several research groups have attempted to use multiple regression analysis to relate the many 'exposure' factors to blood lead (Yankel et al., 1977; Galke et al., 1977; Angle and McIntire, 1979; Charney et al., 1980; Stark et al., 1982). The child-specific factors caused a low correlation for the population studied, and r^2 for multiple regression equations has ranged from 11 to over 50%. The low blood lead relationship to soil lead reported by Barltrop et al. (1975) may have resulted from local cultural factors (cleaning, hand-washing, nutrition), since other populations have higher blood lead per unit dust lead exposure (Duggan, 1983).

Exposure to Heavy Metals in Urban Soils

Baltimore Survey

We undertook a survey of heavy metal levels in gardens in Baltimore because (i) we believed that the safety of garden crops could be evaluated more reliably if we knew the metal concentration in urban garden soils, (ii) we were concerned about lead ingestion by children resulting from family gardening, (iii) we believed sources of metals could be identified if multi-element analyses (fingerprinting) were conducted, (iv) we hoped patterns of pollution within a city would help identify sources and aid Extension Service agents in advising gardeners of the need for soil analysis, and (v) we believed that advisory programmes in other cities could learn from the experiences of a research study, and thus survey their city patterns at lower cost.

Table 4 shows the effect of distance from the city centre on lead levels in garden soils. The mean lead level fell with distance, but some very high lead levels were found in garden soil up to at least 10 miles from the centre. Davies (1978) and Davies et al. (1979) noted the effect of "years of resi-

Table 4.

Effect of distance from the centre of Baltimore on lead concentration ($\mu g\ g^{-1}$) in garden soils*.

Distance (Miles)	Number	Mean	Min.	Max.
0-3	103	964	26	10900
3-5	112	319	11	4990
5-7	99	256	11	7820
7-10	61	70	10	958
10+	101	36	1	382

* Based on data reported by Mielke et al., 1983.

dence" and distance from the centre of London on lead concentration in soils. These data indicated that human activities result in the addition of lead to soils over time. "Distance from the city centre" is almost equivalent to "years of residence" in relation to soil lead accumulation because of the automotive exhaust and paint residues which are the dominant lead sources.

The lead mean for our survey was higher than those of some others because we included the more highly polluted inner-city gardens. If we had separated the inner-city community gardens into individual garden plots, our means would have been even higher. Each garden location was sampled by compositing many subsamples for that whole garden area.

Variability Within Gardens

Table 5 shows results for detailed sampling of three gardens. The gardens were marked into a 3 m x 3 m grid pattern, and a bucket auger (a point sample) of soil was collected at the intersections of the grid. These gardens were community gardens on lots where buildings had been demolished. These results point out the difficulty of sampling urban gardens with respect to the extreme variability. One can afford only so much testing, and we would recommend that gardeners have at least two samples analysed per garden. Each

Table 5.

Variability of heavy metal concentrations ($\mu g\ g^{-1}$) within individual urban gardens.

Parameter	Garden A			Garden B	Garden C
	Pb	Zn	Cd	Pb	Pb
No. samples	111	110	110	72	63
Mean, ppm	740	404	2.45	626	261
C.V., %	56.2	58.2	60.5	70.3	207
Geo. mean, ppm	626	340	2.06	508	171
Median, ppm	640	362	2.16	525	152
Min., ppm	100	70.5	0.48	70	57
max., ppm	2040	1260	9.53	2440	4080
% over 500 $\mu g\ g^{-1}$ Pb	66.4	-	-	51.4	4.8
% over 1000 $\mu g\ g^{-1}$ Pb	25.2	-	-	16.7	1.6

For Garden A:
$Cd = -0.335 + 0.00693\ Zn,\ r^2 = 81.0\%.$
$Cd = -0.944 + 0.00456\ Pb,\ r^2 = 61.1\%.$
$Zn = -111. + 0.693\ Pb,\ r^2 = 66.5\%.$

sample should represent half the area, and be composited from about 20 subsamples evenly spaced in the half garden.

Not only is sampling difficult, but so is interpretation. If 20% of the points in an urban garden contain over 1000 $\mu g\ g^{-1}$ Pb, but the average is less than 500 $\mu g\ g^{-1}$, what advice should be given? If children play in soil at the high lead points, they could be at risk. At this time, there is no comfortable answer for this problem. It is hoped that public health officials will address the risk of variable garden soil lead since they must deal with the much worse case of house-side soils where the lead remains highly concentrated in the surface 0-2 cm of soil. In gardens, metals are mixed into the tilled layer, 0-20 cm deep, and diluted compared with roadside or houseside surface soils.

Sources of Metals from Urban Soils

The main sources of lead in soils include natural occurrences, pesticide additions prior to 1950, smelters, both primary and secondary, including non-ferrous smelters other than lead-zinc smelters, as well as steel works, refuse incinerators, automobiles which pollute roadside soils on a local scale but to high concentrations, and particulates of many sources which occur in urban air. Lead in paint can be added to soil during building demolition, and also from flaking and peeling paint from surfaces of poorly maintained buildings. The practice of using municipal sewage sludge as cropland or domestic garden fertilizer can also result in increased soil levels of lead as well as of other metals. Numerous other minor or very local sources exist for lead in soil. This subject is treated in greater detail by Chaney et al. (1984).

Bioavailability of Food and Soil Lead

After lead is ingested, it can produce health effects only if it is absorbed. A major aspect of childhood lead poisoning is the 50% absorption of ingested lead by susceptible children. Adults usually absorb less than 5% of dietary lead, but can absorb a higher percentage if iron-deficient. Thus both dietary factors and lead source factors may affect whether a particular level of ingested lead is of health significance.

Factors Affecting Lead Absorption by Animals

Researchers have examined dietary factors which affect lead absorption. Mahaffey (1983) recently summarized these findings. Low iron status causes greater lead absorption (see also Flanagan et al., 1979). Low calcium status increases both lead absorption and relative distribution of lead between soft tissues (kidney, blood, etc.) and bone, the normal sink for absorbed lead. Diets low in calories, protein, zinc and vitamin C, or high in fat, tend to increase lead absorption. Chisolm (1981) recently noted interactions among lead, zinc and iron in children.

These results complicate any attempt to evaluate the bioavailability of lead from an environmental source. Further, when rats are fed a nutritionally adequate purified diet, lead absorption is much greater than when the same amount of lead is fed in rat chow. Kostial and Kello (1979) found that the bioavailability of lead added to many human foods was like that of lead added to purified diets. Although lead in paints containing lead pigments was bioavailable to rats fed rat chow, lead octoate was not (Mylroie et al., 1978); when lead octoate was added to a purified complete diet, lead was readily absorbed. Rat chow contains high levels of iron, calcium and fibre compared with National Research Council specified complete purified diets for rats.

Bioavailability of Lead in Soil and Dust

Three research studies on bioavailability of soil or dust lead have been reported. Dacre and Ter Haar (1977) added lead acetate, roadside soil (2300 $\mu g\ g^{-1}$ Pb) or house-side soil (990 $\mu g\ g^{-1}$ Pb) at about 50 $\mu g\ g^{-1}$ added lead to a lab chow type diet for rats, and fed it for 30 or 90 d. Lead in bone and kidney indicated that soil lead was significantly, but slightly, less bioavailable than lead acetate; soil averaged about 70% as available as lead acetate.

Stara et al. (1973) reported studies on bioavailability of street dust lead using a quite different approach, and using purified diets. Bone and blood lead reached much higher levels, and dust lead was about as bioavailable as lead acetate. Relative bioavailability was not computed.

In research at Beltsville, we collected soil from five urban gardens and compared these with control soil and lead acetate in a rat feeding experiment (Table 6). A complete purified casein-sucrose diet was used, and all lead sources were added at 50 mg kg^{-1} dry diet. Addition of 5% uncontaminated soil

Table 6.

Effect of soil on availability of lead to rats, and bioavailability of lead in urban garden soils (Levander, Welsh, Chaney, Mielke, and Leech, unpublished).

Diet*	Pb in Tibia ($g\ g^{-1}$ tibia ash ± SE)	% of Pb Acetate
Basal	0.3 ± 0.3 e**	-
Basal + 5% soil***	0.0 e	-
Basal + Pb acetate	247 ± 10.1 a	100
Basal + Pb acetate + 5% Soil***	130 ± 29.5 bc	53
Basal + 706 $\mu g\ g^{-1}$ Pb soil	40.0 ± 6.1 de	16
Basal + 995 $\mu g\ g^{-1}$ Pb soil	108 ± 26.3 c	44
Basal + 1078 $\mu g\ g^{-1}$ Pb soil	37.1 ± 7.3 de	15
Basal + 1265 $\mu g\ g^{-1}$ Pb soil	53.6 ± 7.4 d	22
Basal + 10240 $\mu g\ g^{-1}$ Pb soil	173 ± 21.8 d	70

* Fed to Fisher rats for 30 days. A purified casein-based complete diet was fed; lead acetate and garden soils were added to supply 50 mg Pb kg^{-1} dry diet.

** Means followed by the same letter are not significantly different ($P \leq 0.05$) according to Duncan's Multiple Range Test.

*** Unpolluted farm soil near Beltsville, MD, similar to original soil in the urban gardens used in this trial.

to the lead acetate diet reduced bone lead by 47%, probably by absorbing lead in the intestine. The bioavailability of garden soil lead ranged from 16 to 70% that of lead acetate; bone lead for two soils was not significantly different than the control, while the highest soil lead level was 70% of, and significantly less than, that of lead acetate.

Although much more research is needed, it appears that the bioavailability of soil lead is related to the concentration of lead in the soil. One would have predicted this result based on metal absorption chemistry. Perhaps this double relationship, i.e. higher lead ingested per unit soil ingested and higher lead bioavailability at higher soil lead, contributes to the general conclusion that soil and dust lead begin to significantly contribute to blood lead when the lead concentration in the soil or dust exceeds 500-1000 μg g^{-1} (EPA, 1977; NAS, 1980; Stark et al., 1982a). Certainly the socio-economic and cultural factors affecting child nutrition can affect the potential blood lead level of children living in environments with high soil and dust lead.

Methods for Soil Metal Analysis

Traditionally, two general types of soil analysis have been used in agriculture. The first is total metals, with use of strong oxidizing acids plus hydrofluoric acid to dissolve silicates. The second is plant-available metals, in which any extractant can be used if plant uptake correlates well with extractable soil metals. These total metal methods require special facilities and safety procedures, and are expensive. Plant-available metal extracts often require special equipment, but use mild reagents with little need for special safety procedures.

Analysis of urban soils, on the other hand, must address the important risk of soil ingestion, not just plant uptake of lead. Although soil factors which affect bioavailability of soil lead to animals have not been well characterized, it is clear that the acid environment of the mammalian stomach can readily dissolve soil lead (Day et al., 1979). Thus, existing research supports the need to use a 'total' method for lead, which is the metal with the most important health risk in urban soils.

Early in our research programme, we recognized the need to identify economically feasible, convenient, and safe soil analysis methods which provided useful soil total lead. Lagerwerff et al. (1973) and others have used 1 N HCl, and 0.1 N HCl has been used to measure plant-available metals in many states. However, when extracting soils with very high lead levels, we found that the limited solubility of $PbCl_2$ could result in underestimation of soil lead when HCl was compared with the results when hot HNO_3 or 1 N HNO_3 were used. John (1971) used a 1 N HNO_3, 2 g soil $(10\ mL)^{-1}$, 30-min extraction to evaluate soil lead.

We also learned that within-sample variability could be a problem in analysing urban soils. Roadside soils, after being crushed and sieved to less than 2 mm (normal preparation for agricultural soil analysis), have a low coefficient of variation because the lead source is finely divided. The lead has accumulated over many years and has equilibrated with the soil. Similar low variation is seen in smelter-polluted soils, and sludge-amended soils after several years. However, house-side soils, or especially soils contaminated by building demolition wastes, contain particulate paint chips. During sieving, one sees and crushes the paint chips to pass the 2-mm sieve. For several years, one can still see the colour of the paint in the chips. The lead-rich particulates cause an intolerable coefficient of variation if small soil samples are required for the method of analysis to be used. Most total methods use small samples, and scientists have ground and/or sieved soils, street dust, etc. to very small particle size before analysis (Day et al., 1975; Day, 1977; Tinsley et al., 1983; Jones and McDonald, 1983).

Thus, we designed a soil total metal analysis method appropriate for analyses of urban gardens and other urban soils (Chaney et al., 1981). We used 5 g of air-dried soil crushed to pass a 2-mm sieve, plus 50 mL of 1 N HNO_3. The slurry is shaken in an oscillating, a wrist-action or a reciprocating shaker for 1 h. Although any clean glass or plastic container could be used, we found that disposable plastic 4-oz. urine specimen containers with screw-cap lids provided a very convenient and inexpensive container, and required no acid-washing before use. The 5 g $(50\ mL)^{-1}$ was selected to provide adequate acid to acidify nearly every conceivable soil, and to provide a filtered solution which allows atomic absorption analysis across a wide range. One can use a turned atomic absorption burner and/or less sensitive lines for analysis of very high soil lead. A 500 µg g^{-1} soil lead yields 50 ppm Pb in the filtered solution (5 g soil $(50\ mL)^{-1}$ acid); this solution would give over 1.0 absorbance at the 217-nm line (0.2 absorbance at 5 ppm with unturned burner), or about half this absorbance at the 283.3-nm line used in lead analysis.

Recommendations for Limiting Heavy Metal Exposure From Urban Garden Soil and Crops

Urban gardeners need to consider both automotive lead emissions and heavy metals in their soil from various other sources. Government could help solve the urban soil pollution problem and prevent it from recurring. Certainly enough research information exists to provide the information/methods to prevent further lead poisoning, etc., related to historical metal pollution of urban soil and dust. The following advice best summarizes practices developed in Boston, MA (McDonough, 1979) and other available information.

An individual can do several general things to protect his/her family:

- prevent pica by children
- obtain soil test for garden or suspect polluted play areas
- provide children a balanced diet with adequate iron and calcium.

If you grow food crops in a garden:

- grow leafy and root vegetables at least 50-100 feet from busy streets
- wash all vegetables to remove soil and dust; peel root crops; discard older or outer leaves during food preparation
- control soil pH near 6.5-7.0; add limestone and organic matter

- if near very heavy traffic, use tall hedges or fences to reduce lead fallout.

If your garden soil analysis indicates lead is over 500-1000 $\mu g\ g^{-1}$:

- replace contaminated soil if possible
- use mulch to reduce soil splash on crops
- wash children's hands, reduce house dust and reduce hand-to-mouth play of young children
- take care to prevent bringing soil into the house on clothes and shoes.

If soil tests very high in lead:

- replace or cover soil
- plant bare areas with grass
- use deep tillage to decrease the lead concentration as a suitable alternative if removal of soil is not possible.

Local government could also help citizens protect themselves and their families from heavy metals in urban soil. Educational programmes could be offered to teach safe gardening practices, and to explain the risks of lead in soil and dust, including house dust. The removal of lead from gasoline could be completed to alleviate this part of the lead risk. Useful soil tests could be offered at the local health department, or at the Land Grant College or University (which usually offers soil fertility tests already). Surveys could be conducted to establish patterns of metal contamination in cities or larger areas (Culbard et al., 1983).

Government agencies could help provide methods to alleviate the urban soil heavy metal problem, by (i) helping identify and replace contaminated soil, (ii) changing zoning to remove demolition debris and contaminated soil and replace with 12 inches of uncontaminated soil, and (iii) determining city-wide patterns of metal pollution and advising local citizens of need for precautions. Although some of these may be expensive, the potential cost to society of a lead-injured child is also very expensive. Citizens may have to communicate their concerns so these problems can be solved soon, before more children are exposed to urban lead.

Several states have prepared Extension Service advisory leaflets regarding lead and gardening in urban areas (e.g. Davies, 1978; McDonough, 1979; McClurg et al., 1979). These provide many of the recommendations noted above. Popular publications have reported these concepts and recommendations (Anonymous, 1981; DeCrosta, 1981; Silverman, 1984). Interested gardeners can contact their local Extension Service representative for advice on this and other gardening problems.

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14. FATE OF GASOLINE LEAD IN THE ENVIRONMENT

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Soil is the overwhelming repository for lead. Like all other trace elements, lead is naturally present in soil, being derived from the weathering of rocks underlying the soil. Swaine (1955) reported that the average lead content of soils is about 16 μg g^{-1}, but that values may range from 1 to 500 μg g^{-1} for soils where crops are normally grown.

A brief calculation shows the large amount of lead available to plants growing on soil containing 16 μg of lead per gram of soil. If we assume that the cultivated depth of a field is about 30 cm and that the density of soil is 1 g cm^{-3}, we can calculate that 1 ha of the cultivated portion of the land contains 4.8×10^{10} μg of lead.

Concentrations of lead in soil are not uniform with depth. Investigators have at times attributed this variation in lead concentration to point or mobile lead sources. In some cases, this lead profile is present even in soils far from industrialization. Wright and co-workers (1955) studied several undisturbed Canadian soils, isolated from industrial areas. These studies showed that lead levels are highest near the surface. This is believed to be a natural process, occurring over thousands of years. The plants absorb lead through the roots, which bring it to the surface where it remains tightly bound to the top soil layer as the plant decays. Some typical data from the Wright et al. paper illustrate this fact (Table 1).

Table 1.

Lead distribution in soil (from Wright et al., 1955).

Soil	Depth (in.)	Lead Concentration ($\mu g\ g^{-1}$)
(1) Brown podzol	Top	28
Brown podzol	0-1	15
Brown podzol	1-4	9
(2) Brown podzol	Top	28
Brown podzol	0-5	6
(3) Brown podzol	Top	108
Brown podzol	0-4	18
(4) Brown forest	Top	23
Brown forest	0-2	19
Brown forest	2-5	18
Brown forest	20+	8

There are two principal barriers hindering the movement of lead in soil to humans via plants:

1) Lead is tightly bound to organic matter in soil and is therefore largely unavailable to plants.

2) Roots absorb and sequester lead, and very little lead is translocated to the upper portions of the plant, which are generally the edible parts.

Lead naturally present in soil, plus those amounts added by man's activities, are chelated by organic (humic) substances present in most soil types. Leaching experiments indicate that lead in soils is not easily removed. For example, Dedolph et al. (1970), in greenhouse experiments found that in soils receiving lead-free water or water containing 40 $\mu g\ L^{-1}$ Pb as lead chloride, the water that percolated through both soils contained less than 1 $\mu g\ L^{-1}$. This indicates that for the situation described by these experiments, lead already fixed in the soil could not be leached from the soil. Moreover, the soluble lead, added as lead chloride, was quickly bound by the soil, since in this case no lead was present in the leachate.

The availability of lead to plants is determined by several factors, e.g. soil pH, the cation-exchange capacity of the soil, the presence of phosphate and carbonate, and soil composition. Regardless of the interaction of these factors, the fact remains that very little of the lead present in soil is taken up by plants. Marten and Hammond (1973) found that an eight-fold increase in total lead content of soil did not increase the lead content of bromegrass. Baumhardt and Welch (1972) grew corn in soils with lead added in amounts ranging from 20 to 100 µg g^{-1} of soil. While lead content of the leaves was significantly greater at about 250 µg g^{-1} (a 2 µg g^{-1} increase over 0 added lead), there was no discernible difference in the lead content of the kernel at any lead concentration studied.

The roots of plants provide a barrier to the movement of lead to the above-ground parts of plants, which are usually the edible portions. Malone et al. (1974) used electron and light microscopy to study corn plants grown in hydroponic solutions containing lead. They found that the roots generally accumulated a surface lead precipitate, and slowly accumulated lead crystals in the cell walls. Lead taken up by the roots was concentrated in dictyosome vesicles, which eventually fused with the cell wall. Only scattered deposits occurred through the stems, and fewer still in the leaves. The addition of phosphorus and lime to soil markedly reduces the uptake of lead by plants (MacLean et al., 1969; Cox and Rains, 1972).

Some investigators have suggested that most of the lead present in plants is due to the use of lead in gasoline. However, the preceding data and experimental studies following suggest that this is not necessarily true. A simple consideration of equilibrium constants explains the observed fact that plants do not readily absorb more lead when lead is added to soil. To ascertain the quantity of lead available to plants, it is important to know the amount of lead in the soil moisture, i.e. dissolved lead. Table 2 shows some examples. Consider a binding constant (K_{sp}) for the lead-soil organic matter complex of 1×10^{-14} and a soil binding capacity of 5×10^{-6} M (moles coordinate). Comparing a natural lead level of 20 μg g^{-1} in soil with a doubled level of 40 μg g^{-1}, the lead in solution increases by only 3%. Likewise, crops grown in the 40 μg g^{-1} soil would be expected to have an increased concentration of no more than 3%. Even increasing lead in soil 10-fold increases lead in solution by only 25%. If the binding or exchange capacity is increased, or the binding constant (K_{sp}) is stronger, effects are even smaller. Only in the case of a low binding constant does lead in solution become appreciable, so that in the case where K_{sp} is 1×10^{-8}, nearly all the lead is in solution. However, this K_{sp} is not realistic, since in practice lead in soil is not easily brought into solution.

Table 2.

Lead in soil solution.

K_{sp}	Moles Coordinate	Mol Pb Present (μg)	Mol Pb in Solution (μg)
1×10^{-14}	5×10^{-6}	1×10^{-7} (20)	2.04×10^{-9} (0.42)
		2×10^{-7} (40)	2.082×10^{-9} (0.43)
		1×10^{-6} (200)	2.499×10^{-9} (0.517)
1×10^{-14}	5×10^{-5}	1×10^{-7} (20)	2.004×10^{-10} (0.0415)
		2×10^{-7} (40)	2.008×10^{-10} (0.0416)
		1×10^{-6} (200)	2.041×10^{-10} (0.0423)

How much lead is added to soil? Data indicate about 1 $\mu g\ cm^{-2}$ Pb occurred in areas in the United States away from major sources (Ter Haar et al., 1967). This was at a time when average lead usage in gasoline was about 2 g per gallon. That figure is of course much lower today. Using 1 $\mu g\ cm^{-2}\ a^{-1}$ and a plow depth for agricultural crops of 30 cm, we can make a comparison of added lead to that already present in the soil. A column of soil 30 cm high and 1 cm^2 contains about 30 g of soil. The average natural lead content is 16 $\mu g\ g^{-1}$. This results in 480 μg Pb in this column. Lead at 1 $\mu g\ cm^{-2}\ a^{-1}$ added to the soil adds only about 0.2%. Even in 100 years, only 3 μg of lead will have been added to the 16 μg naturally present in each gram of soil. When we see that doubling the 16 increases crop levels only by an unmeasurable 3%, it is readily understood why the use of lead in gasoline has no meaningful effect on our food crops.

Studies of lead in soil have shown that the impact of lead is mainly restricted to small areas. Lead has an impact chiefly in three areas: near painted houses, along roads and near point sources. Studies of soils near houses have shown that deteriorated paint is the principal cause of lead in this soil. Ter Haar and Aronow (1974) reported a detailed study of the distribution of lead around urban and rural frame homes and around urban brick homes. Lead concentrations within 2 feet of both the urban and rural frame houses were over 2000 $\mu g\ g^{-1}$. The lead in soil was still elevated at 10 feet from the houses, with an average of 436 $\mu g\ g^{-1}$ present for the urban houses and 609 $\mu g\ g^{-1}$ for the rural. The urban homes, where painted trim is the source of lead, showed much lower levels: averages of 468 $\mu g\ g^{-1}$ at 2 feet and 178 $\mu g\ g^{-1}$ at 10 feet from the house. Figure 1 shows the lead distribution for the urban houses.

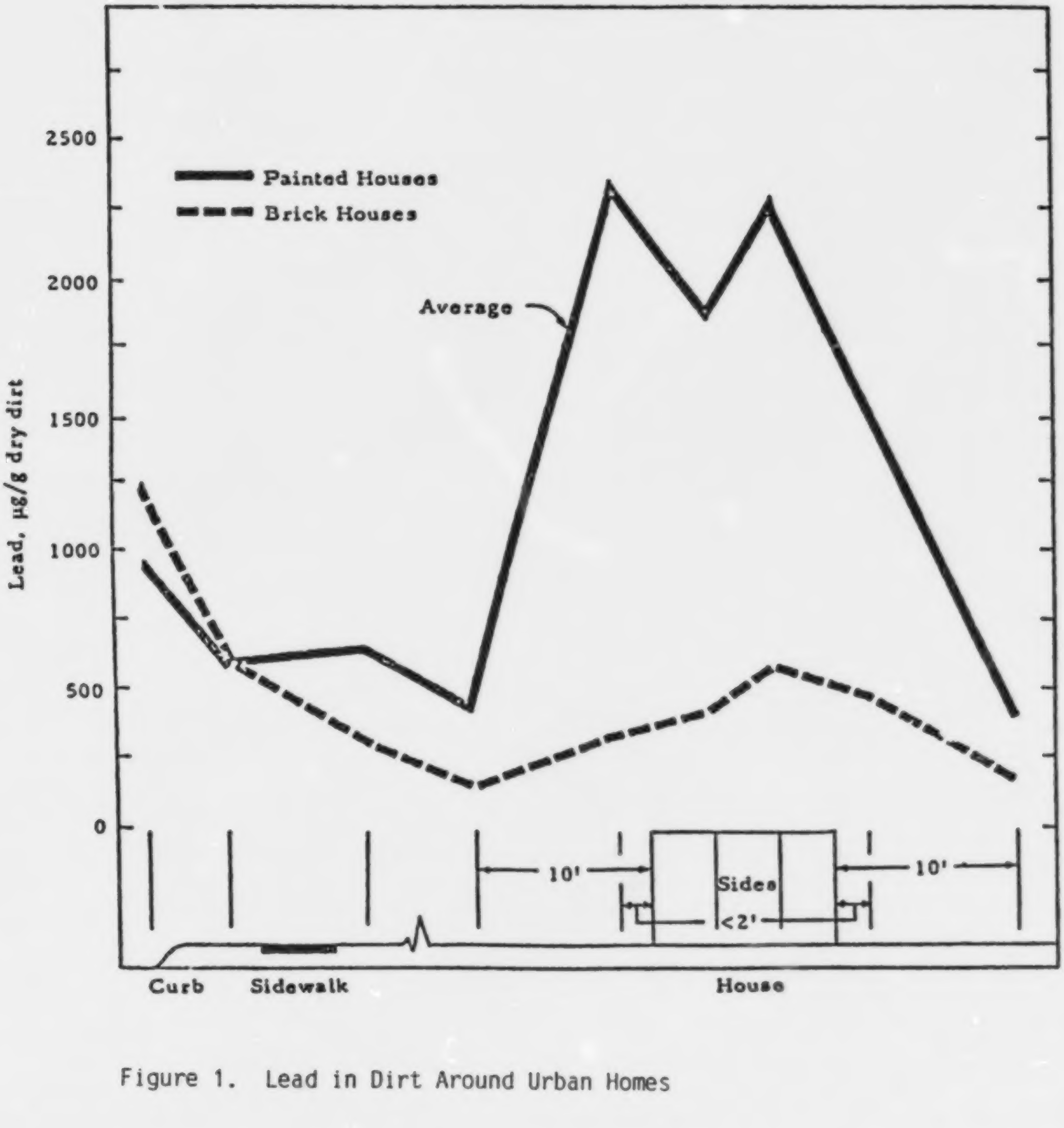

Figure 1. Lead in Dirt Around Urban Homes

Near busy highways and point sources, lead fall-out is high and can contribute to soil levels. Various studies have reported decreasing lead content of soils with increasing distance from the highway and with depth beneath the surface. Data in Table 3 are typical (Lagerwerff and Specht, 1970). There was a reduction of about 65-75% in the lead content of the top 5 cm of soil obtained from 8 m away to 32 m away from a highway with traffic densities ranging from 7500 to 48,000 cars per day.

Table 3.

Lead content in roadside soil as a function of distance from traffic and soil depth (from Lagerwerffe and Specht, 1970).

Site	Distance from Road (m)	Lead Content ($\mu g\ g^{-1}$ dry weight) Soil Profile Layer 0-5 cm	5-10 cm	10-15 cm
West of US 1 near Beltsville, Maryland	8	522	460	416
	16	378	260	104
	32	164	108	69
West of southbound lanes Washington-Baltimore Pkwy., Bladensburg, Maryland	8	540	300	98
	16	202	105	60
	32	140	60	38
West of Interstate 29, Platte City, Missouri	8	242	112	95
	16	140	104	66
	32	61	55	60
North of Seymour Road, Cincinnati, Ohio	8	150	29	11
	16	101	14	8
	32	55	10	6

The data in Table 4 show there is almost no effect beyond 10 m for a road carrying more than 12,000 cars per day, and none beyond 1 m for a road carrying 2000 cars per day (University of Illinois, 1974).

Lead in dust and dirt should be compared with lead in soil. Investigators frequently report high levels of lead in dust and 'dirt' near highways and streets. This 'dirt' is frequently debris collected from the gutter of the street. Dust samples are taken in a similar manner, using perhaps a small brush and paper to collect the sample. The dust samples might be taken in the street, on a porch, inside a building or in any area the investigator chose. These samples will invariably have high concentrations of lead, which are usually only poorly correlated with lead in air or total traffic passing that point. Indeed, lead in dust was high even before lead antiknock additives were widely used. A comprehensive investigation in London in 1930 showed an average of 3500 μg g^{-1} Pb. The authors of the report concluded that lead was universally present in the dust of London and the surrounding districts (HMSO, 1930).

Table 4.

Lead in soil near roads (from University of Illinois, 1974).

Distance from Pavement (m)	Lead in Soil (μg g^{-1} dry wight) 12,000 Cars/24 h	2000 Cars/24 h
1	420	42
5	50	15
10	35	15
15	20	14
20	22	14
25	15	14
30	18	14
40	14	14
50	18	14
75	14	14
100	15	14

These data are typically expressed as concentration (e.g. μg g^{-1}). Values expressed in this manner can be very misleading. For example, in a clean house with almost no dust, a very small amount of lead present will result in a high value for lead concentration, and this has nothing to do with a large amount of lead, but rather relates to the very small amount of dust. Expressing lead values as lead deposited per given area in a given time is a far better method of evaluating lead exposure.

Ter Haar et al. (1981) designed a study to measure this deposition rate near a road carrying 30,000 cars per day. Outdoor samplers were set at 15, 30, 60 and 150 m from the road. The outdoor sampler consisted of a plastic jar with 122.7 cm^2 of area to catch the sample. Each sampler was set on a post about 1.5 m above the ground. The indoor sampler was a plastic pan with a cross-sectional area of 457 cm^2. This pan was set in an area in the house where it would not interfere with daily activities.

Table 5 summarizes the lead fall-out data at various distances from a highway carrying 30,000 cars per day. The indoor rate of fall-out is slightly less at 60 and 150 m than at 15 m. Also, rate of lead fall-out indoors is very low, averaging less than 0.2 $\mu g\ cm^{-2}\ a^{-1}$.

There is a greater effect of the road on the outdoor data compared with the indoor data. Levels at 30 and 60 m are about 70% (30% reduction) of those at 15 m, while the value is about half at 150 m. The lead fall-out rate is about 5-10 $\mu g\ cm^{-2}\ a^{-1}$ which is typical for a residential area (Hunt et al., 1970).

Examination of the last column in Table 5 ($\mu g\ g^{-1}$ Pb) could result in the incorrect conclusion that the exposures to lead inside and outside are the same, and the distance from the road has no effect. The data in $\mu g\ cm^{-2}$ per month obviously give a far clearer picture of the influence of the highway and the marked factor of 35 between lead fall-out rates indoors and outdoors.

Table 5.

Lead fall-out (from Ter Haar et al., 1981).

	Highway Carrying 30,000 Cars Per Day		
	Fall-out ($\mu g\ cm^{-2}$ month)		
Distance from Road (m)	Lead	Total Particulate	Lead ($\mu g\ g^{-1}$)
		Indoors	
15	0.019	18	1055
60	0.014	19	737
150	0.015	15	1000
		Outdoors	
15	0.83	590	1406
30	0.59	590	1000
60	0.54	520	1038
150	0.42	560	1750

These data show that the child in the house will have little exposure to fall-out lead in dust.

The speculation that lead fall-out causes elevated blood lead levels in small children is not borne out by this study. Although it is true that the lead fall-out rate outdoors is somewhat affected by distance from the road, the difference at 15 m and greater distances is not striking. In addition, the fall-out rate indoors is very small. As a child of 1-4 years spends the majority of his time indoors, it is clear that the rate of lead fall-out indoors at either 15 or 150 m from a road carrying 30,000 cars per day is too small to have a measurable effect on the child's blood lead level. This is consistent with the observation of Ter Haar and Chadzynski (1979) in a study of children living at increasing distance from busy roads in Detroit. They reported that the condition of the housing affected the blood lead level, but that distance from the road had no effect on blood lead.

The following conclusions can be made on the subject of lead in soil:

1) Lead concentrations in soil decrease with depth from the surface. This occurs because plants absorb lead through the roots, where it is brought to the surface and bound tightly to the top soil layer as the plant decays.

2) Fall-out data from a time when lead usage in gasoline was 2 g per gallon indicate approximately 1 μg cm^{-2} a^{-1} in areas of the US away from major sources.

3) Lead fall-out is higher near busy highways and point sources where it can contribute to natural soil levels.

4) Lead in paint on homes in rural areas and in large cities contributes to lead in soil around these homes.

Lead in Air: Contribution to Food

Ter Haar (1970) conducted greenhouse studies where lead in air was reduced about 10-fold compared with ambient levels. Also, crops were grown at increasing distances from busy highways, harvested, and lead content was determined. Table 6 shows the concentration of lead in the edible portions of plants grown in the unfiltered and filtered air, with a soil lead level of 17.1 μg g^{-1}. The concentrations of lead in crops grown in unfiltered (1.4 μg m^{-3}) air are essentially the same as the lead content of the plants grown in filtered (0.09 μg m^{-3}) air, except leaf lettuce.

Table 7 shows that increased lead levels in air and soil do not markedly affect the concentration of lead in the edible portions of most crops, but that the inedible parts of the plants (i.e. corn husks, wheat chaff, usually unharvested outer cabbage leaves) and leaf lettuce contained higher concentrations of lead when grown near the road, compared with those grown farther away.

Table 6.

Lead in crops--greenhouse studies (from Ter Haar, 1970).

	Lead ($\mu g\ g^{-1}$ dry weight)	
	Unfiltered Air ($1.45\ \mu g\ m^{-3}$)	Filtered Air ($0.09\ \mu g\ m^{-3}$)
Soil	17.1	17.1
Leaf lettuce	6.6	3.2
Cabbage - Head	1.0	1.1
- Unharvested leaves	4.5	5.8
Tomatoes	0.59	0.72
Beans	1.4	1.2
Bean leaves	20.9	7.9
Sweet corn - Kernel	0.22	0.27
- Cob	0.48	0.69
- Husk	6.9	1.8
Carrots	1.7	2.1
Potatoes	0.30	0.33
Wheat	0.18	0.16

These studies are in agreement with the statement in the UK report Lead and Health (DHSS, 1980) that "Crops grown near airborne sources of lead generally make only a small contribution to the diet and thus to the intake of lead." In addition, Jessup (1978) of the New South Wales Department of Agriculture in one of his conclusions agreed with Zimdahl (1976), who had carried out an extensive research programme in the US on lead in food, that "Airborne lead could contribute only 0.5 to 1.5% of the (lead in the) U.S. diet if all crops were grown near a busy highway."

Table 7.

Lead in crops--highway studies (from Ter Haar, 1970).

Distance from Road (m)	10	40	160
Air (µg m^{-3})	2.3	1.7	1.1
	Lead (µg g^{-1} dry weight)		
Soil	65	40	25
Leaf lettuce	6.5	5.0	4.8
Cabbage - Head	0.56	0.86	0.83
- Unharvested leaves	6.4	8.9	4.0
Tomatoes	1.3	1.2	1.6
Beans	1.9	1.2	0.90
Potatoes	0.48	0.64	0.40
Sweet corn - Kernel	0.39	0.21	0.83
- Cob	0.74	0.55	0.68
- Husk	12.6	6.6	5.7
Soybeans - Beans	0.28	0.12	0.10
- Husks	15.9	8.0	5.3
Oats - Kernel	0.47	-	0.53
- Chaff	31.4	15.5	12.8
Carrots	1.6	-	1.5
Wheat - Kernel	0.62	0.42	0.48
- Chaff	17.8	9.8	6.2

Lead in food comes primarily from processing and from lead naturally present in soils. During past years, food lead measurements indicate a significant reduction from the figure of approximately 300 mg d^{-1} reported in Kehoe's balance studies to levels of 100-150 mg d^{-1} as reported in the seven-city study (Kehoe, 1961; Tepper and Levin, 1972). This reduction has occurred during the period when lead usage in gasoline was greatest, and when the lead naturally present in soils was not changing. Therefore, the reduction is most probably attributable to improved food processing, including:

- more care in making the lead-soldered joints in 'tin' cans
- substitution of glass containers for baby foods, etc.

The foregoing studies, plus other carefully controlled studies, show the following:

1) Food is the most important source of lead in humans.

2) Lead in food comes from naturally occurring lead in the soil and from processing.

3) Lead in air does not affect the edible portion of most plants, but can increase the lead concentration in the non-edible portion.

4) A several-fold increase of lead in soil does not affect the lead content of the edible portion of most plants.

5) Crops grown near airborne sources of lead generally make only a small contribution to the diet and thus to the intake of lead.

UK Survey of Lead in Food Report

This report (UK MAFF, 1983) shows that the lead contents of stable 'foodstuffs' in the UK are generally low and are not increasing. The lead content of total diet in some areas can be elevated due to plumbo-solvent water supplies. The report confirms other studies in which canned foods have higher lead contents due to the processing and lead-based solder from the cans.

The report mentions "an independent estimate of the contribution of fall-out lead to dietary lead intake has also been made by measurement of ^{210}Pb in the diet," but cites no reference for this work. The independent investigator assumed that all of the ^{210}Pb in the food comes from fall-out lead. He then took known data for lead and ^{210}Pb fall-out and estimated the contribution of fall-out lead to lead in food to be "no more than 13 to 16%."

There is a fundamental error in this calculation. ^{210}Pb in food does not come primarily from fall-out lead. Soil contains measurable amounts of ^{210}Pb (1-2 pCi g^{-1}). Thus, there is a ready source of ^{210}Pb in soil. Only a small portion of that comes from fall-out. There is radon in the soil, which does not escape but disintegrates to ^{210}Pb in the soil. Clearly, compact foods (e.g. potatoes, rice and wheat) are not affected by ^{210}Pb fall-out. A reasonable contribution of soil-derived ^{210}Pb to the total ^{210}Pb in food is 90%. Thus, the 13 μg stable lead assigned by the independent investigator to fall-out lead should instead be 1.3 μg (10% x 13). Thus, using the mean lower and upper limits of lead intake of 80 and 100 μg d^{-1} (used in the UK report), the dietary lead from fall-out lead now becomes 1.3-1.6% instead of 13-16%.

The role of dust and dirt in lead intake in children is of high interest. It is appropriate to look at studies that provide considerable information on the contribution of lead from soil, dust and dirt to total lead intake. Barltrop et al. (1975) studied populations in villages with varying amounts of lead in soil in order to determine the significance of increased lead in soil and dust. Blood lead levels in children and their mothers living in rural areas with minimal airborne lead but high levels of lead in dust were reported. The results are shown in Table 8 for both children and mothers.

These results indicate that lead in soil and dust does not influence the adult (mother); however, approximately 1000 μg g^{-1} of lead in soil resulted in an increase in the blood lead level of children of less than 1 μg dL^{-1}. Ter Haar and Aronow (1974) carried out a study using ^{210}Pb, which is a decay product of naturally occurring radon gas, as a tracer or marker for ingested

Table 8.

Soil lead - blood lead relationship (from Barltrop et al., 1975).

Soil Lead ($g\ g^{-1}$)	Blood Lead ($\mu g\ dL^{-1}$) Children	Mothers
1,000	20.7	14.1
1,000 - 10,000	23.8	18.7
10,000	29.0	14.8

dust or soil. The levels of lead and the tracer in normal children and children hospitalized because of suspected excessive lead intake were compared. The data, summarized in Table 9, show that in the children hospitalized because of suspected excessive lead intake, there was no evidence of overt ingestion of dust and dirt, because these children had approximately the same level of ^{210}Pb, the tracer for dust and dirt intake, in faeces in both groups. However, the output of stable lead in faeces was much higher in the group with suspected excessive lead intake, indicating that some lead source other than dust and dirt was responsible for the excessive lead intake; this was most probably lead in paint. These findings are consistent with the findings of Barltrop et al. (1975).

A unique opportunity to quantify the total contribution of airborne lead from both inhalation and fall-out to total lead intake occurred after a major reduction in the lead content of gasoline. This study, conducted in Frankfurt, FRG (Sinn, 1981), compared changes in air lead and blood lead levels of population groups with specific exposure to motor vehicle emissions after the permissible lead content of gasoline was reduced from 0.4 to 0.15 $g\ L^{-1}$. The results are summarized in Table 10. Blood lead analyses were

Table 9.

Lead in ^{210}Pb in faeces (from DHSS, 1980).

	Lead		Lead-210	
	$\mu g\ g^{-1}$	$\mu g\ d^{-1}$	$pCi\ g^{-1}$	$pCi\ d^{-1}$
Normal Children				
Average	3.8	79	0.034	0.680
Range	1.2-8.5	22-174	0.016-0.120	0.252-2.185
Median	3.3	76	0.027	0.583
Lead Children				
Average	111	1781	0.043	0.540
Range	3.9-1640	8-29,030	0.018-0.102	0.072-1.615
Median	18.0	218	0.037	0.298

Table 10.

Frankfurt blood lead study (gasoline lead reduced from 0.4 to 0.15 g L^{-1} in January 1976) (from Sinn, 1981).

	1975/76	1976/77	1977/78
Air Pb ($\mu g\ m^{-3}$)*	3.18	1.04	0.66
Blood Pb ($\mu g\ dL^{-1}$)**			
Erlangen Lab	19.5	18.0	18.4
Berlin Lab	13.4	12.2	11.7
Lostock Lab	16.3	14.6	13.0

Blood Pb ($\mu g\ dL^{-1}$)	1976/77-1975/76	1977/78-1976/77
Erlangen Lab	-1.5	+0.4
Berlin Lab	-1.2	-0.5
Lostock Lab	-1.7	-1.6

*3 m above street with 27,000 vehicles per day.
**n = 215-280 men and women.

carried out by three experienced laboratories: Erlangen, Berlin and Lostock. Because of the significant variation between laboratories, the authors reported results from each laboratory. The air lead level decreased from 3.18 μg m^{-3} in December 1975/January 1976 to 1.04 μg m^{-3} in December 1976/January 1977 (a difference of 2.14 μg m^{-3}), while the blood lead levels decreased by only approximately 1.5 μg dL^{-1}. Sinn (1981) stated that the change in blood lead during this 1-year period was 8.25% for males and 10.25% for females. In addition, there was no significant change for females for the period December 1976/January 1977 to December 1977/January 1978, and the results for males similary remained relatively unchanged.

In conclusion, the contribution to the adult lead intake from the fallout of airborne lead to food, water or other pathways is relatively minor, but this concentration may be slightly greater for children. The data indicate a contribution to blood lead of children of less than 1 μg dL^{-1} for each 1000 μg g^{-1} of lead in soil.

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15. A MODEL OF THE RELATIVE CONTRIBUTION OF ATMOSPHERIC LEAD TO TOTAL HUMAN LEAD EXPOSURE IN THE UNITED STATES

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Introduction

This paper describes a systematic evaluation of the total lead exposure of humans from both natural and anthropogenic sources. The evaluation is a multimedia approach that establishes an intermediate step in modelling the relationship between air lead and tissue lead. The model summarizes the total human exposure to lead from all sources in anticipation that such information can be correctly applied to physiological models that interpret the relationship between lead exposure and tissue lead concentrations. Only those pathways that expose the human body to lead in the human environment are discussed. The model does not attempt to define exposure in natural ecosystems, nor is it concerned with details of the physiological processes affecting the distribution of lead within the human body.

The model distinguishes between natural and anthropogenic lead and attempts to identify anthropogenic lead by source. If a regulatory decision must be based on the relationship between ambient air lead and human health, it is imperative that decisionmakers have the best description of the magnitude of total anthropogenic lead exposure for humans. With a multimedia exposure model, this decision can be based on that fraction of the total exposure that is derived from the atmosphere, from canned food or from other sources more difficult to characterize.

The Approach

For the purposes of this discussion, exposure is defined as the total amount of lead that enters the human body by inhalation or oral consumption. Figure 1 shows the conceptual model of the multimedia approach, identifying four compartments or reservoirs that contribute to the human consumption of lead: air, food, water and dust. Within each reservoir there is a complex mixture of lead from several sources: atmospheric lead in air, food and dust; metallic lead (solder) in food and water; and pigment lead in dust. All of these are in addition to natural lead found in each reservoir. Figure 2 describes the sources of lead and the network of pathways that lead to the four reservoirs of human exposure.

Categories of Lead Exposure

Only a small fraction of the total amount of lead consumed involves inhalation. The model assumes that all inhaled lead is retained in either the lung or stomach. The deposition of particles on the airway surfaces is highly dependent on particle size. Since most lead in air is on particle sizes below 10 µm, inhaled particles are trapped by either the lung tissue or the mucous membranes of the airways. Particles trapped in the airways are passed out to the oesophagus and down to the stomach. The small amount of inhaled lead that is expired is of no significance to the total exposure model.

Much larger amounts of anthropogenic lead are consumed inadvertently as particulate matter added to dust and food. This particulate matter enters the food cycle by wet or dry deposition during growth, harvesting and transportation of crops, and the processing and preparation of food. Similar processes add anthropogenic lead, either atmospheric or otherwise, to dust.

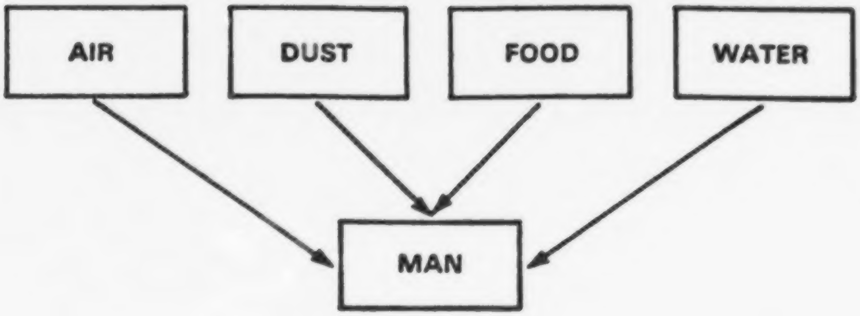
AIR
DUST
FOOD
WATER
MAN

Figure 1. A Simple Model of Human Lead Exposure That Does Not Distinguish Among Sources of Anthropogenic Lead.

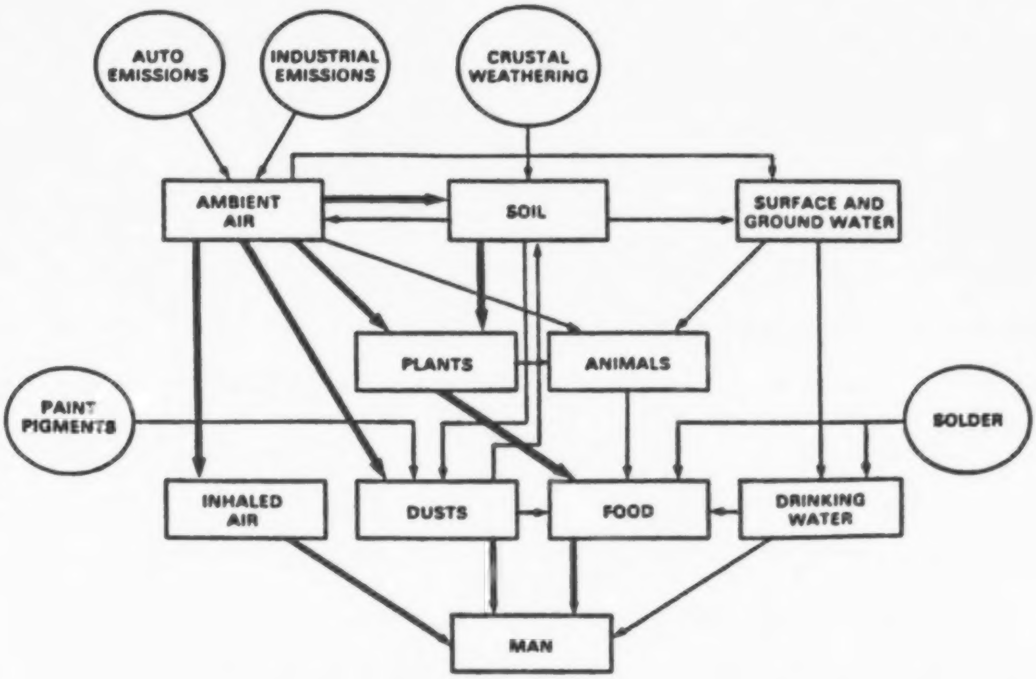
AUTO EMISSIONS
INDUSTRIAL EMISSIONS
CRUSTAL WEATHERING
AMBIENT AIR
SOIL
SURFACE AND GROUND WATER
PLANTS
ANIMALS
PAINT PIGMENTS
SOLDER
INHALED AIR
DUSTS
FOOD
DRINKING WATER
MAN

Figure 2. Exposure of humans to lead from all major sources along the most common environmental pathways. The heavy arrows represent the primary routes of exposure to atmospheric lead.

Sources of Lead

Natural lead occurs in crustal rocks which are weathered to form soils. This lead is transferred to soil moisture in very small amounts, and is taken up by plants, including agricultural crops. A portion of the lead in soil is also of atmospheric origin, and some urban soils also contain large amounts of pigment lead.

Atmospheric lead originates with emissions from mobile and stationary sources. A large fraction (70-90%) of this lead comes from lead additives in gasoline. In the atmosphere, the lead can be found on particulate matter over a wide size range, although particles smaller than 1 µm contain proportionately higher concentrations of lead. Nearly all of the particulate matter inhaled and much of the particulate matter added to food, beverages and dusts are of atmospheric origin. Exposure to metallic lead occurs primarily by the consumption of food in cans with a lead-soldered seam, and of water distributed either in lead pipes or in copper pipes sealed with lead solder at the joints. Normal exposure to pigment lead occurs by the consumption of dust from houses with interior lead paint, or from soil dusts near structures painted with lead-based paint. The consumption of paint chips and the inhalation or consumption of dust from paint removal projects are special cases that are discussed later.

Baseline Exposure

Because it is difficult to define in detail that portion of human lead exposure that can be attributed to natural lead alone, it is more productive to assume some fundamental level of exposure that includes a relatively small amount of natural lead and a consistent anthropogenic lead component. This fundamental level is referred to as the baseline level, beyond which any additional exposure would be a matter of choice, habit or circumstance. At the baseline level, the model for human exposure to lead assumes the individual lives in a non-urban community not proximate to stationary or mobile sources of lead, in a house without lead-based paints, eats a typical diet and engages in no lead-related occupational or avocational activities. The baseline level is not the natural level of lead exposure comparable to what one would expect of pre-historic man, but the presumed lowest level of exposure under normal living conditions. It would be virtually impossible for this person to reduce his level of exposure without extraordinary changes in lifestyle.

The Model

The data that are input to the model are the concentrations of lead in the various components, the amounts of each item in the compartment consumed and the relative fractions of each component that can be attributed to atmospheric and metallic lead. If there is uncertainty concerning the source, the minimum fraction is used, and any exposure beyond the minimum level is attributed to lead of 'undetermined origin.' The model runs on a microcomputer with a custom template adapted to a standard spreadsheet format. Repeated reanalyses of human exposure with the model are possible using any reasonable values to demonstrate increased exposure due to departures from the baseline situation.

Exposure to Lead

$$L_t = L_f + L_a + L_d \qquad (1)$$

The total lead exposure (L_t) is the sum of food and beverage exposure (L_f), air exposure (L_a) and dust exposure (L_d). These components of Eq. (1)

correspond to the four compartments of Figure 1, except that food and water are combined for the convenience of the existing data base. This data base consists of a food consumption study by Pennington (1983) and a corresponding FDA Market Basket Survey (FDA, 1985). Pennington (1983) reported a study of food consumption by eight age/sex groups: infants aged 6-18 months, toddlers aged 2 years, male and female teenagers aged 14-16, male and female young adults aged 25-30, and male and female seniors aged 60-65. The study identified and measured consumption in 231 food categories. These are the same food categories used by the FDA Market Basket Survey. Lead concentration data for 30 categories of baby food are not available, so the first age category is not included in this report.

In each food category, the daily exposure to lead by source is a product of the amount of food consumed in each category and the concentration of lead in that category:

$$L_f = F_1C_1 + F_2C_2 + \ldots.F_nC_n \tag{2}$$

where L_f = total amount of lead consumed in food and beverages ($\mu g\ d^{-1}$)

F_i = amount of food in category (i) consumed ($g\ d^{-1}$)

C_i = concentration of lead in food category (i) ($\mu g\ g^{-1}$)

n = number of food categories (201)

Adjusting for the time spent indoors and outdoors, the exposure due to inhalation is calculated according to Eq. (3):

$$L_a = A_iC_i + A_oC_o \tag{3}$$

where L_a = total amount of lead in inhaled air ($\mu g\ d^{-1}$)

A_i, A_o = volume of air inhaled while indoors or outdoors ($m^3\ d^{-1}$)

C_i, C_o = concentration of lead in indoor or outdoor air ($\mu g\ m^{-3}$)

Lead exposure to dust is estimated as the amount of dust consumed times the baseline concentration of lead in dust (Eq. (4)). Many recent publications that analyse human lead exposure cite a single reference by Day et al. (1975), which concluded that children consume 100 mg of dust per day. In the absence of a better published value, and because it appears to be a very conservative estimate of dust consumption, the same value is used in this model. However, it should be cautioned that much of the sensitivity of the model relies heavily on this assumption. For adults, a value of 20 mg dust is used as the assumed dust consumption.

$$L_d = D_t(C_hP_h + C_sP_s + C_oP_o) \qquad (4)$$

where L_d = total amount of lead consumed in dust ($\mu g\ d^{-1}$)

C_h, C_s, C_o = concentrations of lead in household, street/playground and secondary occupational dust ($\mu g\ g^{-1}$)

P_h, P_s, P_o = fraction of consumed dust attributable to household, street/playground and secondary occupational dust

D_t = total amount of dust consumed from all sources ($g\ d^{-1}$)

To identify the contribution of lead by source within each category, it is necessary to modify Eqs. (2) and (4) by inserting a source coefficient (R_{xn}) for each expression. Equations (5) and (6) are expansions of Eqs. (2) and (4) to account for the source of the lead. Equation (3) was not modified because it is assumed that all inhaled lead is of atmospheric origin. This

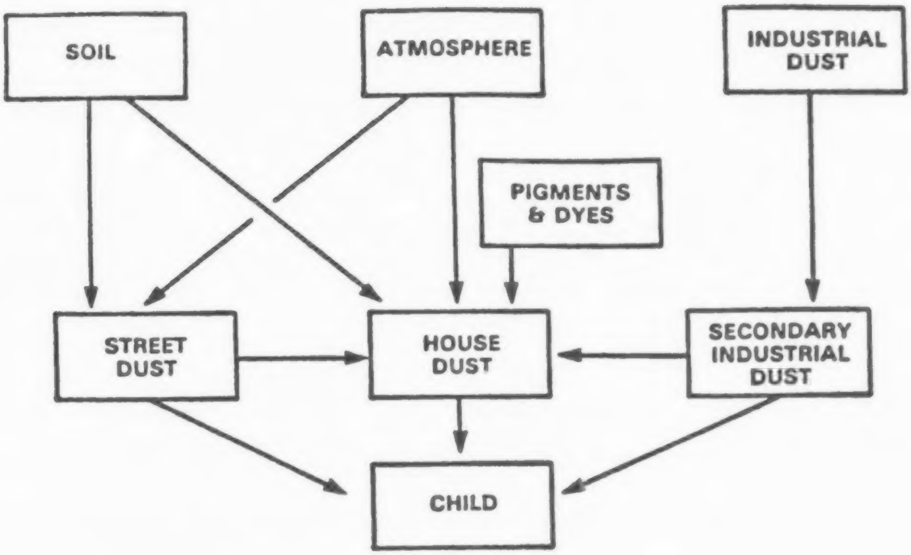
SOIL
ATMOSPHERE
INDUSTRIAL DUST
PIGMENTS & DYES
STREET DUST
HOUSE DUST
SECONDARY INDUSTRIAL DUST
CHILD

Figure 3. A simple model of the sources and pathways of lead in dust. This model demonstrates the three major types of dust in the environment of children, and the complexity of the sources for each type of dust.

Table 1.

Background concentrations of lead in basic food crops and meats. Except as indicated, data are from Wolnik et al. (1983, 1985). Units are in µg g^{-1} fresh weight.

Crop	Natural Lead	Indirect Atmospheric Lead	Direct Atmospheric Lead	Total Lead
Wheat	0.0015	0.0015	0.0340	0.0370
Potatoes	0.0045	0.0045	0.0000	0.0090
Field corn	0.0015	0.0015	0.0190	0.0220
Sweet corn	0.0015	0.0015	0.0000	0.0030
Soybeans	0.0210	0.0210	0.0000	0.0420
Peanuts	0.0050	0.0050	0.0000	0.0100
Onions	0.0025	0.0025	0.0000	0.0050
Rice	0.0015	0.0015	0.0040	0.0070
Carrots	0.0045	0.0045	0.0000	0.0090
Tomatoes	0.0010	0.0010	0.0000	0.0020
Spinach	0.0015	0.0015	0.0420	0.0450
Lettuce	0.0015	0.0015	0.0100	0.0130
Beef (muscle)	0.0002	0.0002	0.0200	0.0204*
Pork (muscle)	0.0002	0.0002	0.0600	0.0604*

*Data from Penumarthy et al. (1980).

Table 2.

Lead consumed in food and beverages. A total of 201 food categories were included, although only a few are shown here for the sake of brevity.

	6-11 mo μg da^{-1}	2 yr μg da^{-1}	14-16 F μg da^{-1}	14-16 M μg da^{-1}	25-30 F μg da^{-1}	25-30 M μg da^{-1}	60-65 F μg da^{-1}	60-65 M μg da^{-1}	AVG FOR AGE GPS μg da^{-1}
Total Pb consumption	13.7	25.1	31.5	45.0	32.1	45.3	32.3	39.8	33.1
Pb from atmospheric sources	4.8	9.4	12.9	18.7	12.9	19.0	12.2	15.6	13.2
Pb from metallic sources	7.3	11.5	12.8	18.8	13.0	18.0	13.8	17.0	14.0
Natural Pb consumption	0.5	1.4	2.0	2.5	2.1	2.8	2.2	2.5	2.0
Pb from indirect atmospheric sources	0.5	1.4	2.0	2.5	2.1	2.8	2.2	2.5	2.0
Pb from undetermined sources	0.6	1.4	1.9	2.6	1.9	2.5	1.9	2.3	1.9
% of total Pb from atmospheric sources	34.6%	37.5%	41.1%	41.5%	40.2%	42.0%	37.8%	39.1%	39.8%
% of total Pb from metallic sources	53.3%	45.8%	40.5%	41.7%	40.7%	39.8%	42.8%	42.7%	42.4%
% of total Pb from natural sources	3.9%	5.5%	6.2%	5.5%	6.6%	6.3%	6.8%	6.2%	6.0%
% of total Pb from indirect atm sources	3.9%	5.5%	6.2%	5.5%	6.6%	6.3%	6.8%	6.2%	6.0%
% of total Pb from undetermined sources	4.3%	5.6%	5.9%	5.7%	6.0%	5.6%	6.0%	5.8%	5.7%

Table 3.

Dust consumed by children and adults. The three types of dust each have different compositions, and are consumed in different amounts. The total amount of dust consumed by children is arbitrarily distributed in the amounts indicated in column two.

Lead Consumed in Dust	Dust Lead ($\mu g\ g^{-1}$)	Dust Ingested ($\mu g\ d^{-1}$)	Lead Consumed ($\mu g\ d^{-1}$)
CHILDREN			
Household dusts	300	0.05	15.0
Street dusts	90	0.04	3.6
Occupational dusts	150	0.01	1.5
TOTAL		0.10	20.1
ADULTS			
Household dusts	300	0.01	3.0
Street dusts	90	0.00	0.0
Occupational dusts	150	0.01	1.5
TOTAL		0.02	4.5

assumption is valid for the baseline situation and most special circumstances except some that involve occupational exposure.

The food crop data, taken at maturity prior to harvest, showed that leafy crops contained more lead than root crops, which were in turn higher in lead than fruits. The root crops in this study are storage organs of photosynthetic products translocated from the leaves. (The fibrous roots that absorb nutrients from the soil are normally higher in lead content than shoots, leaves or fruits, but were not a part of this study). On the assumption that there is some atmospheric lead in all vegetation, the assignment of a source coefficient to Eq. (2) is a two-step process. First, the amount of atmospheric lead in the harvested crop is estimated based on the crop type (leafy vegetable, root vegetable, grain or fruit). Then the amount of lead added during transportation, processing and packaging is determined based on the difference between the FDA Market Basket Survey and the food crop data, and the atmospheric and metallic fractions are estimated. Figure 4 depicts the conceptual model of lead added during the transformation from crops in the field to food on the table. In those cases where packaging occurred without further processing, very little additional lead can be detected. In other cases, additional lead seems to appear in proportion to the approximate time required for processing. The process is similar for meats.

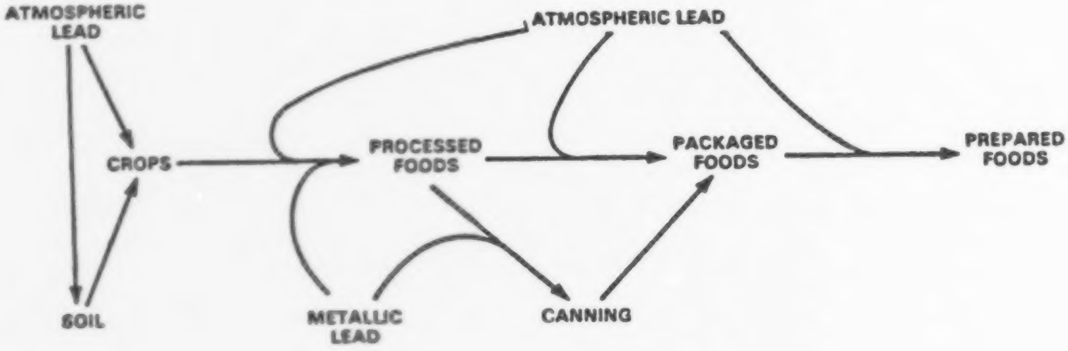
ATMOSPHERIC LEAD
ATMOSPHERIC LEAD
CROPS
PROCESSED FOODS
PACKAGED FOODS
PREPARED FOODS
SOIL
METALLIC LEAD
CANNING

Figure 4. Potential contributions of atmospheric lead to food crops during growth, harvesting, processing, and preparation.

In the several cases where canned fruits and vegetables were analysed separately from their fresh or frozen counterparts, lead in the canned food averaged 0.15 μg g^{-1} higher than uncanned. Between these two sources of anthropogenic lead, nearly all of the added lead could be accounted for, with only a small fraction attributed to lead of undetermined origin. The result is a separate source coefficient for the atmospheric, metallic, natural and undetermined lead for each food and beverage category (Eq. (5)). For added exposure above the baseline situation, there is a source coefficient for pigment lead where paint chips or dust are incorporated into the food preparation process.

$$L_f = F_1C_1R_{a1}+F_1C_1R_{m1}+F_1C_1R_{s1}+F_1C_1R_{u1}+F_2C_2R_{a2}+. . .F_nC_nR_{un} \qquad (5)$$

where R_{an}, R_{mn}, R_{sn}, R_{un} = source coefficients for atmospheric, metallic and soil lead and for lead of undetermined origin for (n) food categories. Soil lead includes natural and indirect atmospheric lead.

There are three general types of dust: street dust, household dust, and secondary occupational dust (Figure 3). Street dust in the baseline situation includes playground dust, and is assumed to contain lead from the soil and the atmosphere (Table 3). There does not yet appear to be a linear or curvilinear relationship between air lead and dust lead concentrations. Therefore, data are substituted empirically into the model from published values of lead in dust where air lead concentrations are known. In non-baseline situations, street dust also contains pigment lead from exterior house paint and lead from nearby industrial activities, but this lead is conceptually excluded by the definition of the baseline situation. On the other hand, household dust is a mixture of soil lead and atmospheric lead, but includes a component of pigments and dyes from a variety of other sources that must be considered an integral part of the typical home. Secondary occupational dust in the baseline situation contains soil and anthropogenic lead in a composition that varies with each home environment. Consequently, most of the lead in occupational dust is of undetermined origin.

$$L_d = D_t[C_hP_hR_{ah}+C_hP_hR_{rsh}+C_hP_hR_{uh}+C_sP_sR_{as}+\cdot\ \cdot\ \cdot C_oP_oR_{uo}] \qquad (6)$$

where $R_{ah}\cdot\ \cdot\ \cdot R_{uo}$ = source coefficients for lead in household, street, or occupational dust representing the contribution of atmospheric and soil lead, and lead of undetermined origin.

Results

Baseline Exposure

Food and beverage exposure may be found in Table 2, and daily exposure to lead in dust is given in Table 3 for children and adults. The total exposure, a summation of inhaled lead, food and beverage lead and dust lead, is shown in Table 4. The baseline parameters discussed above suggest that over 60% of the lead consumed daily by children in a baseline situation is of atmospheric origin. The atmospheric fraction is higher for children because of the presumed amount of dust consumed. Much of the remaining lead comes from the solder in food cans. About 6% is of natural origin, and 3-4% is of undetermined origin. In the baseline situation it is likely that most of the lead of undetermined origin is either atmospheric or metallic lead.

In the baseline form, this model focusses clearly on the sources of lead that comprise the greatest exposure to humans. Because the baseline para-

Table 4.

A summary of the total baseline exposure of humans to lead by source and age/sex group.

Exposure	Intake ($\mu g\ d^{-1}$) by Age (years)						
	2 y	14-16		25-30		60-65	
		F	M	F	M	F	M
AIR	0.5	1.0	1.0	1.0	1.0	1.0	1.0
FOOD & BEVERAGES							
Atmosphere	9.4	12.9	18.7	12.9	19.0	12.2	15.6
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Indirect Atmospheric	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Undetermined	1.4	1.9	2.6	1.9	2.5	1.9	2.3
Total food & beverages	25.1	31.5	45.0	32.1	45.3	32.3	39.8
DUST							
Atmosphere	17.9	4.1	4.1	4.1	4.1	4.1	4.1
Metallic	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Natural	1.5	0.3	0.3	0.3	0.3	0.3	0.3
Indirect atmospheric	0.5	0.1	0.1	0.1	0.1	0.1	0.1
Undetermined	0.2	.0	.0	.0	.0	.0	.0
Total dust	20.1	4.5	4.5	4.5	4.5	4.5	4.5
TOTAL EXPOSURE							
Atmospheric	27.8	18.0	23.7	17.9	24.1	17.2	20.6
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	2.9	2.3	2.8	2.4	3.1	2.5	2.8
Indirect atmospheric	1.9	2.1	2.6	2.2	2.9	2.3	2.6
Undetermined	1.6	1.9	2.6	2.0	2.6	2.0	2.3
Total air, food & dust	45.7	37.0	50.5	37.6	50.8	37.8	45.3
% Atmospheric	60.9%	48.7%	47.0%	47.8%	47.4%	45.6%	45.5%
% Metallic	25.1%	34.5%	37.2%	34.7%	35.5%	36.5%	37.5%
% Natural	6.3%	6.1%	5.5%	6.4%	6.2%	6.6%	6.1%
% Indirect atmospheric	4.1%	5.6%	5.1%	5.9%	5.8%	6.0%	5.7%
% Undetermined	3.5%	5.1%	5.2%	5.2%	5.1%	5.2%	5.2%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

meters are carefully selected to exclude additional lead exposure, the model demonstrates the lowest achievable lead exposure in the United States without unreasonable changes in life-style.

The model does not establish baseline parameters. The baseline parameters were inserted into the model from the available literature and can be changed if the conditions or assumptions change. This flexibility allows the potential for predicting lead exposure under expected conditions in the future, or exposure in countries with food consumption habits similar to those of Americans. The model is also not limited to lead exposure. If the required data are available, they may be inserted in the same manner as the lead data, assuming there are no other routes of exposure, such as dermal absorption.

Additional Exposure

In order to predict exposure beyond the baseline level, it is necessary to estimate the change in parameters for the 'above baseline' situation. For example, an urban child would breathe the same amount of air and consume the same amount of dust, but with a higher concentration of lead (e.g. 1.5 versus 0.1 $\mu g\ m^{-3}$ for air, and 1000 versus 300 $\mu g\ g^{-1}$ for dust) in each case. Food consumption would probably remain the same, although the argument could be made that kitchen preparation in an urban situation may add more lead than that in a rural location. Inserting these changes in the model for baseline exposure gives the new exposure (Table 5). If the family also lives in a house with lead-based paint, the household dust level might increase to 2000 $\mu g\ g^{-1}$, giving a total exposure profile as indicated in Table 6.

Summary

This model uses a flexible structure that is amenable to changes in either the baseline information or formulae for calculation. The output is informative from the standpoint of presenting timely summaries of changes in exposure with any departure from the baseline situation, and changes to the baseline exposure expected from any modification of ambient air quality.

Table 5.

A summary of total exposure for an urban family. In his departure from the baseline situation, the air lead concentration has been changed from 0.1 to 1.5 μg m^{-3}, the household dust from 300 to 1000 μg g^{-1} and the street dust from 90 to 1500 μg g^{-1}.

	Intake (μg d^{-1}) by Age (years)						
Exposure	2 y	14-16		25-30		60-65	
		F	M	F	M	F	M
AIR	7.5	15.0	15.0	15.0	15.0	15.0	15.0
FOOD & BEVERAGES							
Atmospheric	9.4	12.9	18.7	12.9	19.0	12.2	15.6
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Indirect atmospheric	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Undetermined	1.4	1.9	2.6	1.9	2.5	1.9	2.3
Total food & beverages	25.1	31.5	45.0	32.1	45.3	32.3	39.8
DUST							
Atmospheric	108.4	11.0	11.0	11.0	11.0	11.0	11.0
Metallic	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Natural	1.5	0.3	0.3	0.3	0.3	0.3	0.3
Indirect atmospheric	0.5	0.1	0.1	0.1	0.1	0.1	0.1
Undetermined	1.1	0.1	0.1	0.1	0.1	0.1	0.1
Total dust	111.5	11.5	11.5	11.5	11.5	11.5	11.5
TOTAL EXPOSURE							
Atmospheric	125.3	38.9	44.7	38.9	45.0	38.2	41.6
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	2.9	2.3	2.8	2.4	3.1	2.5	2.8
Indirect Atmospheric	1.9	2.1	2.6	2.2	2.9	2.3	2.6
Undetermined	2.5	2.0	2.7	2.0	2.7	2.0	2.4
Total air, food & dust	144.1	58.0	71.5	58.6	71.8	58.8	66.3
% Atmospheric	87.0%	67.2%	62.4%	66.4%	62.7%	64.9%	62.7%
% Metallic	8.0%	22.0%	26.3%	22.3%	25.1%	23.5%	25.6%
% Natural	2.0%	3.9%	3.9%	4.1%	4.4%	4.2%	4.2%
% Indirect Atmospheric	1.3%	3.6%	3.6%	3.8%	4.1%	3.9%	3.9%
% Undetermined	1.7%	3.4%	3.8%	3.5%	3.7%	3.5%	3.6%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Table 6.

Total lead exposure for an urban family living in housing with lead-based paint. In addition to the urban family changes made for Table 5, the household dust has been changed to 2000 μg g^{-1}. This dust is pigment lead, which shows up as lead of undetermined origin because there is no special category for pigment lead.

	Intake (μg d^{-1}) by Age (years)						
Exposure	2 y	14-16		25-30		60-65	
		F	M	F	M	F	M
AIR	7.5	15.0	15.0	15.0	15.0	15.0	15.0
FOOD & BEVERAGES							
Atmospheric	9.4	12.9	18.7	12.9	19.0	12.2	15.6
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Indirect atmospheric	1.4	2.0	2.5	2.1	2.8	2.2	2.5
Undetermined	1.4	1.9	2.6	1.9	2.5	1.9	2.3
Total food & beverages	25.1	31.5	45.0	32.1	45.3	32.3	39.8
DUST							
Atmospheric	103.9	10.1	10.1	10.1	10.1	10.1	10.1
Metallic	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Natural	1.5	0.3	0.3	0.3	0.3	0.3	0.3
Indirect atmospheric	0.5	0.1	0.1	0.1	0.1	0.1	0.1
Undetermined	55.6	11.0	11.0	11.0	11.0	11.0	11.0
Total dust	161.5	21.5	21.5	21.5	21.5	21.5	21.5
TOTAL EXPOSURE							
Atmospheric	120.8	38.0	43.8	38.0	44.1	37.3	40.7
Metallic	11.5	12.8	18.8	13.0	18.0	13.8	17.0
Natural	2.9	2.3	2.8	2.4	3.1	2.5	2.8
Indirect atmospheric	1.9	2.1	2.6	2.2	2.9	2.3	2.6
Undetermined	57.0	12.9	13.6	12.9	13.6	12.9	13.3
Total air, food & dust	194.1	68.0	81.5	68.6	81.8	68.8	76.3
% Atmospheric	62.2%	55.9%	53.7%	55.4%	54.0%	54.2%	53.3%
% Metallic	5.9%	18.8%	23.0%	19.0%	22.0%	20.1%	22.3%
% Natural	1.5%	3.3%	3.4%	3.5%	3.8%	3.6%	3.6%
% Indirect Atmospheric	1.0%	3.0%	3.2%	3.2%	3.6%	3.3%	3.4%
% Undetermined	29.4%	18.9%	16.7%	18.9%	16.6%	18.8%	17.4%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

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16. TRANSPORT OF LEAD FROM THE ENVIRONMENT TO MAN

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Introduction

During the development of nuclear power, many calculations were made of the transfer of radioactive nuclides by various pathways from air and water to man. Sometimes the calculations were done before the event materialized: for example, the transfer of ^{131}I from air to herbage, and so to milk and to man, was defined by experiment and calculation several years before the Windscale accident in 1957 provided a large-scale demonstration. With lead, the hazards to health have been known and experienced for centuries, but it is only in recent years that the controversy over lead in petrol has given the incentive to study experimentally the pathways of lead to man. For lead, as for many radioactive species, the tie-up between experiment and experience is made easier by the possibility of assessing the body burden--or at least a significant part of it--in the living subject. For this reason, epidemiological evidence is much more abundant, and human experiments more rewarding with lead than with elements such as cadmium, for which the degree of uptake is much more difficult to assess. Also, lead has four stable isotopes (204, 206, 207, 208) and four radioactive isotopes (203, 210, 212, 214), all of which except one occur naturally; this provides fascinating possibilities for elucidating the pathways leading to human uptake.

Inhalation Pathway

This mode of uptake is fairly well understood, thanks in large part to the experiments of Kehoe which first defined the problems. Ambient lead aerosol particles may vary in size from 0.01 to 10 μm or larger. In general, the smaller the size, the greater the fractional capture in the lung of the inhaled aerosol and the greater the likelihood of absorption of the lead into the blood.

Experimental inhalations of stable and radioactive lead aerosols, and epidemiological surveys (Kehoe, 1961; Griffin and Knelson, 1975; Gross, 1981; Chamberlain, 1983a, 1985; Royal Commission on Environmental Pollution, 1983), have given reasonably consistent results for the response of blood lead (PbB, μg dL^{-1}) to exposure to air lead (PbA, μg m^{-3}). The experiments with stable lead aerosols, and the epidemiological surveys, show the effect on PbB of increasing exposure to PbA and measure α, which is the slope of curve relating PbB to PbA. Experiments with isotopes (including the Isotopic Lead Experiment (ILE) experiment in Italy), in which the subject's total uptake of lead is not significantly increased by the experiment, measure β, which is the contribution to PbB from exposure to PbA. α and β have the same units (μg dL^{-1} per μg m^{-3}), and are identical if the response of PbB to uptake of lead is linear, but not otherwise. There is evidence (Chamberlain, 1983a, b) that $\alpha = \beta$ if PbB is less than 20 μg dL^{-1}, but α is less than β when PbB becomes larger.

Experimental inhalations of aerosols labelled with ^{203}Pb, together with other data on deposition of aerosols in the lung, lead to the conclusions:

$\beta \approx 2$ μg dL^{-1} per μg m^{-3} for particles of about 0.04 μm in diameter

$\beta \approx 1$ μg dL^{-1} per μg m^{-3} for particles of about 2 μm in diameter

The above apply when the period of exposure is of the order of months. For longer exposure, β may increase, due to resorption into blood of lead previously stored in bone, perhaps by 30% over several years.

Dust Pathway

As particle size increases, deposition and uptake in the lung become less effective. Also, the ratio of indoor to outdoor PbA becomes less (Roberts et al., 1974a, b). The importance of direct absorption of dust, especially by young children, then increases. The EPA favours an 'aggregate approach' by which lead in house dust (PbD, mg g^{-1}) and lead in garden soil (PbS, mg g^{-1}) are considered to be related to PbA so that a standard can be set for PbA which takes into account uptake of dust. Experience in Britain and the Netherlands does not altogether support this approach. High levels of PbS in Britain are mostly related to historical causes: fall-out from former industrial emissions and spread of domestic debris. The intake by young children of house dust containing lead from old paint cannot be distinguished from intake from licking painted objects. Insofar as PbD and PbS are related to current fall-out and so to PbA, the best parameter may be not PbD or PbS itself but the rate of fall-out (mg m^{-2} d^{-1}), which may be denoted PbF.

Brunekreef et al. (1983) found that PbF, measured outdoors near the home, was the best predictor of PbB for Dutch children (4-6 years old). After adjustment for other variables, there was a regression equivalent to an increase of 5 µg dL^{-1} in PbB per 1 mg m^{-2} d^{-1} in PbF, i.e.

$$\Delta \text{PbB} = 5\ \text{PbF}$$

This relation appears to work reasonably well when applied to the situation near smelters, where very high PbF values (associated with relatively large particle sizes) have been reported. Roberts et al. (1974a, b) found PbF =

2 mg m^{-2} d^{-1} at 300 m from 'smelter B' in Toronto, and this would imply an excess PbB of about 10 μg dL^{-1} in children living very close to the smelter.

Roels et al. (1980) measured PbF near a lead smelter in Belgium, and found values as high as 19 mg m^{-2} d^{-1} at 500 m, reducing to 6 mg m^{-2} d^{-1} at 700 m and 2 mg m^{-2} d^{-1} at 1 km. Roels et al. found a mean ΔPbB of 15 μg dL^{-1} in 11-year-old children living less than 1 km from the smelter (1978 values). There was a high level of lead on the hands, and Roels et al. showed that this, and not PbA, was the reason for the elevated PbB. Both the Toronto and Belgium data appear reasonably consistent with the relation between PbB and PbF found by Brunekreef et al. (1983).

In Turin, where motor traffic is dense and meteorological dispersion poor, PbA was estimated at 1.7 μg m^{-3} and PbF at 0.7 mg m^{-2} d^{-1} (Facchetti and Geiss, 1982; Colombo and Fantechi, 1983). The isotopic ratio of the street dust was found to be nearly the same as that of the airborne particulate. Using ΔPbB = 2 PbA + 5 PbF, a contribution of 7 μg dL^{-1} to children's blood lead from inhalation and ingestion of dust would be expected. The isotopic analysis of children's blood in Turin showed that about one-third was derived from gasoline lead. The mean PbB of children was 16 μg dL^{-1}, so the actual effect appears slightly less than expected.

The alternative method of predicting the contribution of dust is to use regressions of PbB on PbD and PbS, and it has been suggested that the relationship:

$$\Delta PbB = 6.8\ PbD + 7.2\ PbS$$

based on the data of Angle and McIntire (1970), and Angle et al. (1984) should be adopted.

In London, England, mean PbD = 1.0 and mean PbS = 0.65 mg g^{-1} (Thornton et al., 1985); applying the above regression, a contribution of 12 μg dL^{-1} to PbB of children would be expected. This is greater than the total PbB currently found, of which a considerable fraction is attributed to dietary intake. The village of Shipham, Somerset, is in an old mining area, and the soils have PbS averaging 3 mg g^{-1} compared with 0.3 mg g^{-1} in a control village, North Petherton. Children in the two villages were found to have mean PbB of 9.5 and 9.4 μg dL^{-1}, respectively (Royal Commission on Environmental Pollution, 1983), whereas the regression derived from Angle and McIntire (1970) and Angle et al. (1984) would have predicted an excess of about 20 μg dL^{-1} in Shipham. It has been suggested that the data from Shipham, and earlier results from Derbyshire, should be disregarded, because the soil in both areas is calcareous. Human experiments on uptake of ^{203}Pb from the gut (Flanagan et al., 1982; Heard and Chamberlain, 1982, 1983; James et al., 1985) have shown that $CaCO_3$ in amounts up to 100 mg Ca per dose is not effective in reducing uptake of lead, unless accompanied by equimolar amounts of phosphate. It seems more likely that deposited lead becomes less available for direct ingestion after the elapse of time, possibly because particles become agglomerated.

Crop Pathway

Foliar Uptake

The entry of airborne radioactive nuclides into diet via fall-out onto crops has been studied very actively since the 1950s, when the fall-out of ^{90}Sr from bomb tests caused concern. The isotope ^{210}Pb is formed naturally in the atmosphere as a decay product of radon, and is deposited, mainly in rain, on all continental areas. Some estimate of the contribution to diet of fall-out of stable lead onto crops can be made by comparing the specific activity of fall-out in agricultural areas. Measurements at Harwell (Chamberlain, 1983b) agree with those previously published from New York (Bogen et al., 1976), and give a specific activity of about 10 nCi g^{-1} in diet and excreta. A similar result was found for faecal excretion of children (1-3 years old) in Detroit (Ter Haar and Aronow, 1974). By comparison, the specific activity of ^{210}Pb in fall-out, in well-populated country areas, is about 100 nCi g^{-1}. In remote continental areas, it is higher. Thus there is evidence (subject to some reservations) that country-wide fall-out of lead onto crops in well-populated areas may contribute about 10% of the total dietary intake of lead (Chamberlain, 1983b). Combining this pathway with the direct uptake of urban dust-fall would give, very approximately:

$$\Delta PbB = 2\ PbA + 5\ PbF + 20\ PbF'$$

where PbF' refers to the rate of fall-out (mg m^{-2} d^{-1}) in the region in which the individual's food is grown. The multiplier applied to PbF' is very uncertain, but the values above are in reasonable accord with the data on ^{210}Pb and also with the response in country districts of Piedmont in the ILE.

Calculations of this type give rather frightening estimates of ΔPbB for the hypothetical individual who lives very close to a smelter or major motorway and grows all his vegetables in his back garden (Royal Commission on Environmental Pollution, 1983), but in Britain no such individual with excessive PbB has in fact been described in the literature.

The pathway of direct foliar uptake may be more effective in far-northern climates, where plants grow slowly and are exposed to fall-out for longer periods (Chamberlain, 1970). High levels of ^{210}Pb have been found in plants, animals and humans living in the Arctic areas of Europe, USA and Canada (Holtzman, 1978). Apart from exceptional situations, the fall-out of stable lead in remote regions is likely to be low, so the enhanced efficiency of the pathway of foliar uptake is probably of little consequence.

Root Uptake

In Britain, smelting and the industrial and domestic use of lead since the 1700s have led to its widespread dissemination, and the mean PbS in topsoil in country districts (0.04 mg g^{-1} dry weight) is higher than in deeper horizons. Industrial emissions have been reduced in the last 50 years, and the fall-out of lead from vehicles has not added appreciably to the soil burdens except close to major roads. Recent experimental work on uptake of lead from soil by vegetables, using ^{210}Pb tracer, has shown that the concentration factor (CF):

$$CF = \frac{\text{Pb per kg dry weight of crop}}{\text{Pb per kg dry weight of soil}}$$

is usually less than 5×10^{-3} (Chamberlain, 1983b; Tracey et al., 1983; Harrison, 1986),with two reservations:

- some plants, for example radishes, seem to have excessive uptake
- with leafy crops, it is very difficult to exclude the contamination of leaves with soil, much of which is removed, however, by washing or by discarding outer leaves before cooking.

The average daily consumption of vegetables in Britain is 280 g fresh weight, equivalent to about 40 g dry weight, so if PbS = 0.04 mg g^{-1} and CF is less than 5×10^{-3}, the probable daily intake of lead derived from vegetables by root uptake from the soil is less than 10 μg d^{-1}. This is small compared with the lead which enters food during manufacture and storage, and the lead in drinking water. A duplicate diet survey at Shipham where the soil lead is very high (Royal Commission on Environmental Pollution, 1983; Sherlock et al., 1983) showed average intake within normal limits, despite PbS levels about 3 mg g^{-1} and considerable use of home-grown vegetables.

Other Sources of Lead in Diet

In the last few decades, in most developed countries, vigorous efforts have been made to reduce the lead contamination of food and drink. The latter is very important, and the only source of lead uptake which is clearly reflected in Britain by epidemiological surveys (Royal Commission on Environmental Pollution, 1983). One reason is that uptake of lead often is very much higher when it is ingested without food (Heard and Chamberlain, 1982). Improvements in water supplies, reductions in the use of lead solder in cans and numerous other measures have all helped. Gross (1981), analysing Kehoe's (1961) data, noted that the average dietary intake of lead by volunteers in Cincinatti halved (from 300 to 150 μg d^{-1}) between 1937 and 1970, a period during which the use of lead in gasoline greatly expanded. It is unlikely that this decrease represented improvements in analytical techniques, because Kehoe from the start of his work took great care to check analysis by independent methods. In Wales, Elwood (1983) and Elwood and Toothill (1986) found evidence of a decline of PbB of about 10% per annum during a period (1970-84) in which lead levels in petrol in the UK remained constant.

Future Research

The following appear particularly in need of further investigation:

1) Duplicate diet studies, to measure the intake of lead in vegetables, in areas of high lead fall-out, similar to that done at Shipham in an area of

high PbS but low PbF.

2) Investigation of a possible pathway from lead in gasoline to the driver or passenger in the car itself, that is not related to the ambient PbA.

3) Measurements of PbB in venous (not capillary) blood from infants and their mothers in areas of high environmental lead. It is suggested (Chamberlain, 1983a) that an increase above about 1.3 in the ratio of child/adult PbB indicates a pathway, such as ingestion of dust or paint, particularly affecting infants.

4) More human experiments on deposition of lead aerosol in the lung, particularly for particle sizes greater than 1 µm not covered in previous work (Kehoe, 1961; Gross, 1981; Chamberlain, 1985). This could be done in the ambient environment, without artificial exposure, wherever PbA exceeds about 2 $\mu g\ m^{-3}$, by measuring PbA in the inhaled and exhaled breath.

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